2021 Spring

# "Phase Equilibria in Materials"

03.31.2021 Eun Soo Park

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Office: 33-313 Telephone: 880-7221 Email: espark@snu.ac.kr Office hours: by an appointment Contents for previous class CHAPTER 4 Binary Phase Diagrams <u>Three-Phase Equilibrium Involving Limited Solubility of the Components</u> in the Solid State but Complete Solubility in the Liquid State

4.3. Three-Phase Equilibrium : Peritectic Reactions

2) Eutectoid reaction

3) Peritectic reaction

Formation of intermediate phases by peritectic reaction

Non-stoichiometeric compounds

4) Congruent transformations

## According to the condensed Phase Rule, f = c - p + I

For a binary system the equilibria possible are summarized below.

Number of components	Number of phases	Variance	Equilibrium	
c = 2	p = 1	f = 2	bivariant	p = c - 1
c = 2	p = 2	f = 1	monovariant	p = c
c = 2	p = 3	f = 0	invariant	$\underline{p} = c + 1$

Invariant reactions which have been observed in binary diagrams are listed below, together with the nomenclature given to such reactions.

 $\begin{array}{l} l \rightleftharpoons \alpha + \beta \\ \gamma \rightleftharpoons \alpha + \beta \\ l_1 \rightleftharpoons \alpha + l_2 \\ \alpha + l_2 \end{array} \qquad \begin{array}{l} \text{eutectic reaction} & (e.g. \text{ Ag-Cu system}) \\ \text{eutectoid reaction} & (e.g. \text{ C-Fe system}) \\ \alpha \rightleftharpoons \beta + l \\ l + \alpha \rightleftharpoons \beta \\ \alpha + \beta \rightleftharpoons \gamma \\ l_1 + l_2 \rightleftharpoons \alpha \end{array} \qquad \begin{array}{l} \text{eutectic reaction} & (e.g. \text{ Ag-Li system}) \\ \text{eutectoid reaction} & (e.g. \text{ Ag-Li system}) \\ \text{eutectoid reaction} & (e.g. \text{ Cu-Zn system}) \\ \text{eutectoid reaction} & (e.g. \text{ Al-Cu system}) \\ \text{eutectoid reaction} & (e$ 

Invariant reactions involving liquid phases have a name ending in *\_tectic* while those occurring completely in the solid state end in *\_tectoid*.

## **Peritectic reaction**

#### Considerable difference between the melting points



Fig. 61. Effect of increasingly positive departure from ideality in changing the phase diagram from a continuous series of solutions to a peritectic-type.



Fig. 43. Effect of increasingly positive departure from ideality in changing the phase diagram for a continuous series of solutions to a eutectic-type.

## **Peritectic reaction**

- Surrounding or Encasement: During peritectic reaction,  $L + \alpha \longrightarrow \beta$ , the beta phase created surrounds primary alpha.
- Beta creates diffusion barrier resulting in coring.







Figure 8.19

#### 4.3.4. Formation of intermediate phases by peritectic reaction



Fig. 68. Formation of an intermediate phase,  $\beta$ , by peritectic reaction.

β: different crystal structure with those of the component older literature\_ intermediate phases ~regarded as a chemical compounds Thus, called intermetallic compounds but, cannot expect from valency considerations & not fixed composition (different with chemical compounds)

## \* Intermediate phases

(1) Size-factor compounds ~ relatively large size differences of the constituent atoms

- e.g. a) Laves phases, which are intermediate phases based on the formula AB<sub>2</sub>, where atom A has the larger atomic diameter.
  - b) Interstitial compounds: metal carbides, nitrides and borides

(2) Electron compounds ~ similar electrochemical properties and a favorable size-factor occurs at one of three valency electron-to-atom ratios.

- e.g. a) 3:2 electron compounds CuZn, Cu<sub>3</sub>Ga, and Cu<sub>5</sub>Sn different %Cu, same electron concentration and similar crystal structure (BCC)
  - **b)** 21:13 electron compounds γ brass (complex cubic lattice with 52 atoms per unit cell)
  - c) 7:4 electron compounds close-packed hexagonal structure similar to  $\varepsilon$  brass

(3) Normal valency compounds (partly-ionic compounds) ~ obey the valency rules

e.g. Mg<sub>2</sub>Si, Mg<sub>2</sub>Sn, Mg<sub>2</sub>Pb and Mg<sub>3</sub>Sb<sub>2</sub>/ much common in ionic compounds such as NaCl and CaF2

### 1) Peritectic point virtually coincides with the liquid composition. But, thermodynamically, points P and b is not possible to coincide.



Peritectic point and the liquid composition are so close to each other that the experimental techniques used were not able to distinguish them. More refined methods would be expected to produce evidence of a <u>compositional difference these two points</u>. 8 2) Decreasing solubility of Zn in Cu with rise in temperature in contrast to the normal decrease in solubility with fall in temperature



Due to an equilibrium with a <u>disordered intermediate phase</u> (e.g. the  $\beta$  phase above 454 °C, Fig. 71)

This has been explained as being due to a greater relative movement of the free energy curve of the intermediate phase compared with the  $\alpha$  solid solution with rise in temperature. <sup>9</sup>

### 4.3.5. Non-stoichiometeric compounds



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#### 4.4 Congruent phase transformations

# Congruent vs Incongruent

#### **Congruent phase transformations: no compositional change associated** with transformation

**Examples:** 

- Allotropic phase transformations
- Melting points of pure metals
- Congruent Melting Point \_\_\_\_\_

#### Incongruent phase transformation: at least one phase will experience change in composition

#### **Examples:**

- Melting in isomorphous alloys
- Eutectic reactions
- Pertectic Reactions
- Eutectoid reactions



## 4.4. Congruent transformations

#### **Congruent transformation:**

(a): a melting point minimum, a melting point maximum, and a critical temperature associated with a order-disorder transformation

(b), (c) and (d): formation of an intermediate phase (next page)



Fig. 76. Examples of congruent transformations.

## 4.4. Congruent transformations

b. More usual type of congruently-melting intermediate phase



Fig. 78. Phase diagram with a congruent intermediate phase.

→ Partial phase diagram A-X and X-B



Microstructure of a cast AI-22% Si alloy showing polyhedra of primary Si in eutectic matrix

: Similar with eutectic alloy system/ primary β phase with well-formed crystal facets (does not form dendrite structure)

In many cases, X = normal valency compound such as Mg<sub>2</sub>Si, Mg<sub>2</sub>Sn, Mg<sub>2</sub>Pb or Laves phase, particularly stable compounds <sup>13</sup>

#### b. More usual type of congruently-melting intermediate phase



Contents for today's class

CHAPTER 5 Binary Phase Diagrams Limited Solubility in Both the Liquid and Solid State

1) Limited Solubility in Both the Liquid and Solid State

2) Monotectic reactions

3) Syntectic reactions

#### 1) Limited Solubility in Both the Liquid and Solid State

### So far, complete miscibility in the liquid state and limited solid solubility

partial solubility even in the liquid state

Free energy and activity curves for (a) kT/C<0.5, (b) kT/C=0.5 (c) kT/C>0.5



 $\Delta G_m = NCX_A(1 - X_A) + NkT[X_A \ln X_A + (1 - X_A) \ln (1 - X_A)]$ 

where,  

$$C = z \left[ H_{AB} - \frac{H_{AA} + H_{BB}}{2} \right]$$
: energy term



\* The curves with *kT/C* < 0.5 show two minima, which approach each other as the temperature rise.

\* With kT/C  $\geq$  0.5 there is a continuous fall in free energy from  $X_A=0$  to  $X_A=0.5$  and  $X_A=1.0$  to  $X_A=0.5$ . The free energy curve thus assumes the characteristic from one associates with the formation of homogeneous solutions.

> • Exactly the same treatment could have been applied to liquid solutions.

Fig. 14. Variation of free energy with composition for a homogeneous solution with  $\Delta H_m > 0$ . Free energycomposition curves are given for various values of the parameter kT/C.

# Effect of very large positive deviations from ideality in changing the phase diagram from a eutectic to a monotectic reaction



#### **Eutectic reaction:** Liquid $\leftrightarrow \alpha + \beta$

Monotectic reaction: Liquid1 ↔ Liquid2+ solid

The reversible transition, on cooling, of a liquid to a mixture of a second liquid and a solid 18



## 2) Monotectic Phase Diagram



G.A. Chadwick, Brit. J. App. Phys., 16 (1965) 1096

# Monotectic

Source: Reed-Hill, Abbaschian, **Physical Metallurgy Principles, 3rd Edition**, *PWS Publishing Company*, 1994.



#### Hypo-monotectic:

Interdendritic divorced eutectic between an α dendritic matrix Slow cooing: Two layers ~ Cu-rich liquid L1 top layer / Pb-rich liquid L2 bottom layer (Rapid quenching: droplet structure)  $\rightarrow$ At T<sub>M</sub>, L1 – monotectic reaction/ L2 –  $\alpha$  precipitates  $\rightarrow$ At T<sub>E</sub>, top:  $\alpha$  + pools of divorced eutectic/ bottom: small particles of  $\alpha$  in a divorced eutectic matrix 21

# Morphology in monotectic solidification



Figure 2. Solid-liquid interface morphology for different interfacial energy conditions: (a)  $\gamma_{S_1L_2} > \gamma_{S_1L_1} + \gamma_{L_1L_2}$ , (b)  $\gamma_{S_1L_2} = \gamma_{S_1L_1} - \gamma_{L_1L_2} \cos \theta$ , (c)  $\gamma_{S_1L_1} > \gamma_{S_1L_2} + \gamma_{L_1L_2}$ .

## **Case 1:** $\gamma_{\alpha l_1} + \gamma_{l_1 l_2} < \gamma_{\alpha l_2}$



Hg-Te single crystal

# **Case 2:** $\gamma_{\alpha l_2} = \gamma_{\alpha l_1} - \gamma_{l_1 l_2} \cos \theta$



Growth mechanism of alloy of monotectic composition to produce a fibrous structure

$$\lambda \propto V^{-0.5}$$



D.A. Porter and K.E. Eastering, "Phase Transformations in Metals and Alloys"

## 4.1.3. Heterogeneous nucleation

From 
$$\Delta G^* = \left(\frac{16\pi\gamma_{SL}^3 T_m^2}{3L_v^2}\right) \frac{1}{(\Delta T)^2}$$
  
Nucleation becomes easy if  $\gamma_{SL}$  t by forming nucleus from mould wall.  
Fig. 4.7 Heterogeneous nucleation of spherical cap on a flat mould wall.  
 $\gamma_{ML} = \gamma_{SL} \cos\theta + \gamma_{SM}$   
 $\cos\theta = (\gamma_{ML} - \gamma_{SM})/\gamma_{SL}$   
 $\Delta G_{het} = -V_S \Delta G_v + A_{SL}\gamma_{SL} + A_{SM}\gamma_{SM} - A_{SM}\gamma_{ML}$   
In terms of the wetting angle ( $\theta$ ) and the cap radius (r) (Exercise 4.6)  
 $\Delta G_{het} = \left\{-\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma_{SL}\right\} S(\theta)$   
where  $S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2/4$   
 $26$ 

#### S(θ) has a numerical value $\leq$ 1 dependent only on θ (the shape of the nucleus)



#### S(θ) has a numerical value $\leq$ 1 dependent only on θ (the shape of the nucleus)



## The Effect of $\Delta T$ on $\Delta G^*_{het} \& \Delta G^*_{hom}$ ?



Fig. 4.9 (a) Variation of △G\* with undercooling (△T) for homogeneous and heterogeneous nucleation.
 (b) The corresponding nucleation rates assuming the same critical value of △G\* 29

### **Barrier of Heterogeneous Nucleation**



#### How about the nucleation at the crevice or at the edge?



### How do we treat the non-spherical shape?



**Good Wetting** 

## **Bad Wetting**

$$\Delta \boldsymbol{G}_{sub}^{*} = \Delta \boldsymbol{G}_{homo}^{*} \left( \frac{\boldsymbol{V}_{A}}{\boldsymbol{V}_{A} + \boldsymbol{V}_{B}} \right)$$

### Effect of good and bad wetting on substrate



Fig. 85. Derivation of the monotectic phase diagram from the free energy curves for the liquid,  $\alpha$  and  $\beta$  phases.

#### \* Limiting forms of monotectic phase diagram



Fig. 86. Limiting form of the monotectic phase diagram.

The solubility is so small as to be undetected experimentally to date.

#### \* Limiting forms of monotectic phase diagram



### **Syntectic reaction**: Liquid1+Liquid2 $\leftrightarrow \alpha$



This reaction will proceed at the interface between the two liquid layers. ~ difficult to maintain equilibrium conditions in a syntectic system



Fig. 87. Syntectic phase diagrams. (a) Schematic: (b) the K-Zn system. e.g. K-Zn, Na-Zn, K-Pb, Pb-U and Ca-Cd
**Contents for today's class** 

\* Monotectic reaction:







\* Syntectic reaction:

Liquid1+Liquid2  $\leftrightarrow \alpha$ 



K-Zn, Na-Zn, K-Pb, Pb-U, Ca-Cd





### **Contents for previous class**

### **Review of Invariant Binary Reactions**

Positive  $\Delta H_m$ 



#### Review of Invariant Binary Reactions *Eutectic* Type Eutectic Al-Si, Fe-C ß $| = \alpha + \beta$ Eutectoid Fe-C ζβ $\vee$ $\gamma \overrightarrow{\phantom{\alpha}} \alpha + \beta$ Monotectic Cu-Pb را 🗸 $|_1 \overrightarrow{\alpha} \alpha + |_2$ Monotectoid Al-Zn, Ti-V ζβ $\alpha_1$ $\alpha_2 \overrightarrow{\phantom{\alpha}} \alpha_1 + \beta$

On cooling one phase going to two phases Metatectic reaction:  $\beta \leftrightarrow L + \alpha$  Ex. Co-Os, Co-Re, Co-Ru

### **Review of Invariant Binary Reactions**

Peritectic Type



On cooling two phases going to one phase

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### **Contents for previous class**

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Positive  $\Delta H_m$ 



#### **Barrier of Heterogeneous Nucleation**



#### How about the nucleation at the crevice or at the edge?

#### How do we treat the non-spherical shape?



**Good Wetting** 

#### **Bad Wetting**

$$\Delta \boldsymbol{G}_{sub}^{*} = \Delta \boldsymbol{G}_{homo}^{*} \left( \frac{\boldsymbol{V}_{A}}{\boldsymbol{V}_{A} + \boldsymbol{V}_{B}} \right)$$

#### Effect of good and bad wetting on substrate

**Contents for today's class** 

### Chapter 6 Binary Phase Diagrams: Reactions in the Solid State

- \* Eutectoid reaction:  $\alpha \leftrightarrow \beta + \gamma$
- \* Monotectoid reaction:  $\alpha_1 \leftrightarrow \beta + \alpha_2$
- \* Peritectoid reaction:  $\alpha + \beta \leftrightarrow \gamma$

### Chapter 7 Binary Phase Diagram: Allotropy of the Components

- \* SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE
- \* SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE
  - \* Metatectic reaction:  $\beta \leftrightarrow L + \alpha$  Ex. Co-Os, Co-Re and Co-Ru

#### Chapter 6 Binary Phase Diagrams: Reactions in the Solid State

~ Only the kinetics of the reaction differ

**Eutectoid reaction:**  $\alpha \leftrightarrow \beta + \gamma$ 

Monotectoid reaction:  $\alpha_1 \leftrightarrow \beta + \alpha_2$ 

**Peritectoid reaction:**  $\alpha + \beta \leftrightarrow \gamma$ 

\* Transformation can only proceed if  $-\Delta G_{bulk} > +\Delta G_{interface} + \Delta G_{strain}$ By nucleation and growth mechanism ~ Strain energy factor

~ nucleation sites of transformation

Disordered atomic arrangement at <u>grain boundaries</u> will reduce the strain energy factor and the interfacial energy needed to nucleate a new phase.

The finer the grain size, and hence the larger the grain boundary area, the more readily will the transformation proceed. "allotropic transformation"







## **Iron-Carbon System**



### Iron Carbon Phase Diagram

**Eutectoid reaction:**  $\gamma \leftrightarrow \alpha + Fe_3C$ 



## **Cementite – What is it?**

Iron Carbide – Ceramic Compound

Purple: Carbon atoms Orange: Iron atoms



- <u>Cementite has an orthorhombic lattice</u> with approximate parameters 0.45165, 0.50837 and 0.67297 nm.
- There are twelve iron atoms and four carbon atoms per unit cell, corresponding to the formula Fe<sub>3</sub>C.

Source: http://www.msm.cam.ac.uk/phase-trans/2003/Lattices/cementite.html H. K. D. H. Bhadeshia

# Pearlite: What is it?



• The eutectoid transformation:

 $\gamma (0.77\% \text{ C}) \rightarrow \alpha (0.02\% \text{ C}) + \text{Fe}_3 \text{C} (6.67\% \text{ C})$ 

- Alternate lamellae of ferrite and cementite as the continuous phase
- <u>Diffusional Transformation</u>
- <u>"Pearlite" name is related to the regular array of the lamellae in colonies.</u> Etching attacks the ferrite phase more than the cementite. The raised and regularly spaced cementite lamellae act as diffraction gratings and a <u>pearl-like luster</u> is produced by the diffraction of light of various wavelengths from different colonies

# Pearlite

• Two phases appear in definite ratio by the lever rule:

$$\alpha = \frac{6.67 - 0.77}{6.67} \approx 88\%$$
  
cementite =  $\frac{0.77 - 0}{6.67} \approx 12\%$ 

- <u>Since the densities are same (7.86</u> and 7.4) lamellae widths are 7:1
- Heterogeneous nucleation and growth of pearlite colonies – but typically grows into only 1 grain



**Fig. 18.6** Pearlite consists of plates of  $Fe_3C$  in a matrix of ferrite. (Vilella, J. R., *Metallographic Technique for Steel*, ASM Cleveland, 1938.) 2500X.

Reed-Hill, Abbaschian, 1994, [5]

### Lamellae Nucleation



Fig. 18.7 The two primary methods of nucleating pearlite. (A) Nucleation of pearlite at an austenite grain boundary (Pitsch-Petch relation). (B) Nucleation of pearlite at a grainboundary layer of cementite (Baryatski relation).

Reed-Hill, Abbaschian, 1994

### **Lamellae Nucleation**



Fig. Growing cementite and ferrite lamellae may nucleate each other.

Reed-Hill, Abbaschian, 1994

### **Eutectic Solidification (Kinetics)**

If  $\alpha$  is nucleated from liquid and starts to grow, what would be the composition at the <u>interface</u> of  $\alpha/L$  determined?

→ rough interface (diffusion interface) & local equilibrium

How about at  $\beta/L$ ? Nature's choice? Lamellar structure

$$\rightarrow$$
 G = G<sub>bulk</sub> + G<sub>interface</sub> = G<sub>0</sub> +  $\gamma$  A

+  $\gamma \mathbf{A}$   $\sum A_i \gamma_i + \Delta G_s = minimum$ 



What would be a role of the <u>curvature</u> at the tip?

→ Gibbs-Thomson Effect

## **Interlamellar Spacing**

- Interlamellar spacing  $\lambda$  is almost constant in pearlite formed from  $\gamma$  at a fixed T.
- Temperature has a strong effect on spacing lower T (large  $\Delta T$ ) promotes smaller  $\lambda$ .
  - Pearlite formed at 700°C has  $\lambda \sim 1 \text{ mm}$  and Rockwell C 15.
  - Pearlite formed at 600°C has  $\lambda \sim 0.1$  mm and Rockwell C 40.
- Zener and Hillert Eq. for spacing (eq. 4.39):

$$\lambda = \frac{4\sigma_{\alpha/Fe_{3}C}T_{E}}{\Delta H_{V}\Delta T}$$

IH6: derive  $\lambda$  with maximum growth rate at a fixed  $\Delta T$  (eutectic case)

- $\sigma_{a/Fe_3C}$  = Interfacial energy per unit area of a/Fe<sub>3</sub>C boundary
- $T_E$  = The equilibrium temperature (Ae<sub>1</sub>)
- $\Delta H_V$  = The change in enthalpy per unit volume
- $\Delta T$  = The undercooling below Ae<sub>1</sub>

## Effect of Undercooling on $\lambda$



Krauss, <u>Steels</u>, 1995

## **Effect of Interlamellar Spacing**



FIG. 16-Yield strength and hardness versus pearlite interlamellar spacing [49].

Stone et al, 1975

## Iron-Carbon (Fe-C) Phase Diagram





### Proeuctectoid Ferrite – Pearlite



0.38 wt% C: Plain Carbon – Medium Carbon Steel



Fig. 93. The monotectoid reaction in the Ta-Zr system (schematic).

 $\beta Zr \leftrightarrow \alpha + \beta Ta$ 

Both βZr and βTa have the <u>same crystal structure</u> (b.c.c.) but different lattice spacing.





Fig. 94. The monotectoid reaction in the Al-Zn system (schematic). (a) Previously accepted phase diagram; (b) recently proposed modification.

## Both $\alpha$ and $\alpha'$ are face-centered cubic phases, differing only in lattice spacing.

#### **Peritectoid reaction:** $\alpha + \beta \leftrightarrow \gamma$

Peritectic

 $| + \beta \overrightarrow{=} \alpha$ 





Cu-Al phase diagram

**Revision of Cu-Al phase diagram** 









Fig. 97. (a) A part of the Cu-Sn phase diagram (after G. V. RAYNOR; courtesy Institute of Metals); (b) equilibrium relationships if the data in (a) are considered limiting cases of the peritectoid and sutectoid reactions.

#### **CHAPTER 7**

### **Binary Phase Diagrams. Allotropy of the Components**

Several commercially important metals exist in more than one crystalline form.

**Ex. Iron**- three allotropes  $\alpha$ ,  $\gamma$ ,  $\delta$ 

Titanium – two allotropes close-packed hexagonal α Ti stable at low temp. and bodycentered cubic β Ti stable at high temp.

Plutonium – six allotropes \_ the highest number of modifications



- a. SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE Such systems can be further divided according to whether the <u>high</u> <u>temperature allotrope forms a continuous series of solid solutions with the</u> <u>other component or not</u>.
  - 7.1.1. The high temperature phase forms a series of solid solutions with the other component



7.1.1. The high temperature phase forms a series of solid solutions with the other component

Types of phase diagrams formed when the high temperature allotrope forms a continuous series of solid solutions with the second component.

(a) single component have two allotropic modifications.





allotropic modification

allotropic modification

7.1.1. The high temperature phase forms a series of solid solutions with the other component (a) single component have two allotropic modifications.



Fig. 99. Cooling of alloys through the  $\beta$  loop.
7.1.1. The high temperature phase forms a series of solid solutions with the other component

(b) Both components have two allotropic modifications.





7.1.1. The high temperature phase forms a series of solid solutions with the other component

(b) Both components have two allotropic modifications.



Fig. 100. The Ti-Zr phase diagram (schematic).

Complete series of solid solutions are formed between each of the allotropes in the system Ti-Zr.

#### a. SYSTEMS IN WHICH ONE PHASE IS IN EQUILIBRIUM WITH THE LIQUID PHASE

7.1.2. Both phases form limited solid solutions with the other component



High-temperature  $\beta$  phase, as well as the low-temperature  $\alpha$  phase form <u>limited solid solutions with component B</u>.

**Polymorphism:** the ability of a solid material to exist in more than one form or crystal structure (Both  $\alpha$  and  $\beta$  are allotropes of A)

**Eutectoid reaction:**  $\alpha \leftrightarrow \beta + \gamma$ 

**Peritectoid reaction:**  $\alpha + \beta \leftrightarrow \gamma$ 



Simple eutectic system with solid-soild phase transitions

b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE

 $L + \alpha \& L + \beta \text{ or } L + \beta \& L + \gamma \text{ or } L + \gamma \& L + \delta$ 



Fig. 102. Examples of phase diagrams in which both allotropes are in equilibrium with the melt.

**Metatectic reaction:**  $\beta \leftrightarrow L + \alpha$  Ex. Co-Os, Co-Re and Co-Ru<sup>3/</sup>

#### **Metatectic reaction:** $\beta \leftrightarrow L + \alpha$ Ex. Co-Os, Co-Re and Co-Ru

(Both  $\alpha$  and  $\beta$  are allotropes of A)



Fig. 103. The metatectic reaction.

#### **Metatectic reaction:** $\beta \leftrightarrow L + \alpha$ Ex. Co-Os, Co-Re and Co-Ru



Fig. 104. Derivation of the metatectic phase diagram (Fig. 103) from the free energy curves for the liquid,  $^{9}$   $\alpha$  and  $\beta$  phases.

## b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE L+ $\alpha$ & L + $\beta$ or L + $\beta$ & L + $\gamma$ or L + $\gamma$ & L + $\delta$



40

### b. SYSTEMS IN WHICH TWO PHASES ARE IN EQUILIBRIUM WITH THE LIQUID PHASE L+ $\alpha$ & L + $\beta$ or L + $\beta$ & L + $\gamma$



#### Review of Invariant Binary Reactions *Eutectic* Type Eutectic Al-Si, Fe-C ß $| = \alpha + \beta$ Eutectoid Fe-C $\vee$ **ζ**β $\gamma \overrightarrow{\phantom{\alpha}} \alpha + \beta$ Monotectic Cu-Pb را 🗸 $|_1 \overrightarrow{\alpha} \alpha + |_2$ Monotectoid Al-Zn, Ti-V $\alpha_1$ **(**β $\alpha_2 \overrightarrow{\phantom{\alpha}} \alpha_1 + \beta$

On cooling one phase going to two phases Metatectic reaction:  $\beta \leftrightarrow L + \alpha$  Ex. Co-Os, Co-Re, Co- $\overset{42}{Ru}$ 

# **Review of Invariant Binary Reactions**

Peritectic Type



On cooling two phases going to one phase

## MIDTERM: 23rd April (Friday) 2 PM - 5 PM,

## 33 Dong 330 & 331 Ho

st I will post your designated seat in front of the classroom on the day of the test.

Scopes: Text ~ page 117/ Teaching note ~10 and Homeworks

## **Eutectic Solidification (Kinetics)**

If  $\alpha$  is nucleated from liquid and starts to grow, what would be the composition at the <u>interface</u> of  $\alpha/L$  determined?

→ rough interface (diffusion interface) & local equilibrium

How about at  $\beta/L$ ? Nature's choice? Lamellar structure

$$\rightarrow$$
 G = G<sub>bulk</sub> + G<sub>interface</sub> = G<sub>0</sub> +  $\gamma$  A

+  $\gamma \mathbf{A}$   $\sum A_i \gamma_i + \Delta G_s = minimum$ 

Interface energy + Misfit strain energy



What would be a role of the <u>curvature</u> at the tip?

→ Gibbs-Thomson Effect

## **Eutectic Solidification**

### How many $\alpha/\beta$ interfaces per unit length?





α

For an interlamellar spacing, λ, there is a total of (2/λ) m<sup>2</sup> of α/β interface per m<sup>3</sup> of eutectic (단위 부피당계면 E).





**Gibbs-Thomson effect** 

 $cf) r^* = \frac{2\gamma_{SL}}{\Delta G_V} = \left(\frac{2\gamma_{SL}T_m}{L_V}\right) \overline{\Delta}$ 

 $L_v$ : latent heat per unit volume  $L = \Delta H = H^L - H^S$ 

#### \* Growth Mechanism: Gibbs-Thomson effect in a ∆G-composition diagram?



The cause of G increase is the curvature of the  $\alpha/L$  and  $\beta/L$  interfaces arising from the need to balance the interfacial tensions at the  $\alpha/\beta/L$  triple point, therefore the increase will be different for the two phases, but for simple cases it can be shown to be  $\frac{2\gamma_{\alpha\beta}V_m}{\lambda}$  for both.

**1)** If  $\lambda = \lambda^*$ , growth rate will be <u>infinitely</u> <u>slow</u> because the liquid in contact with both phases has the same composition,  $X_E$  in Figure 4.32.



 $(\Delta X)$ . (b) Model used to calculate the growth rate.

## $\Delta X$ will it self depend on $\lambda$ . ~ maximum value, $\Delta X_0$

