Phase Diagram

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Objectives

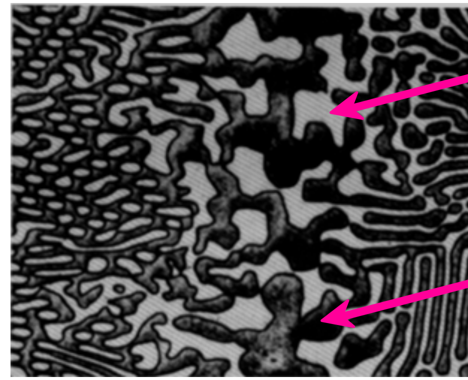
- 단순한 전율고용체(isomorphous)와 공정(euetectic) 상태도(phase diagram)의 개략도 작성
  - 상태도의 상구역 표시
  - 액상선, 고상선 및 솔버스선 표시
- 2원계 상태 이해 및 다음의 세가지를 결정(determine) 할 수 있는 rule 이해
  - 주어진 조건 (T,C)에서 어떤상이 존재하는지?
  - 존재하는 상의 조성
  - 존재하는 상들 간의 무게 분율 (wt%)
- 2원계 (binary system) 상태도에서 다음 사항 determine
  - 공정 (eutectic), 공석 (eutectoid), 포정 (peritectic) 및 정융 (congruent) 변태의 온도와 조성
- 철-탄소 합금 상태도 이해
  - 아공석 (hypoeutectoid), 과공석 (hypereutectoid)
  - 초석상 (proeutectoid)
  - 초석상과 펄라이트 무게 분율 산출
  - 공석 반응 바로 아래 온도에서의 개략적 미세조직

Introduction

- 미세조직(microstructure)는 기계적 성질 (mechanical property)와 밀접한 관계
- 한 합금의 미세조직은 그 합금의 상태도에 나타나는 다양한 정보로써 짐작 가능하다.
- 따라서 상태도에 쓰여있는 정보들을 잘 이해하는 것이 중요.
- 상태도 (phase diagram)?
  - 한 물질의 상(phase)을 온도/압력/조성에 따라 나타낸 도형 (diagram)
  - 주로 압력을 제외하고 (고정된 압력) 온도/조성에 따라 물질의 '평형상'을 나타낸다.
- Terminology
  - 합금 (alloy)
  - 상 (phase): 물리적,화학적 성질이 균일한 계의 균질한 부분 (예: 설탕물)
  - 평형 (equilibrium); 시간에 따라 바뀌지 않고 유지 (상평형: 1개 이상 상이 존재하는 계의 평형; tl간에 따라 변하지 않는다.)
  - 성분 (Component): 합금을 구성하는 순금속이나 화합물 (예: 황동의 성분은 구리와 아연)
  - 계 (System):
    - 1. 고려 대상 물질의 집합체;
    - 2. 합금의 조성에 관계없이 같은 성분 요소로 이루어진 합금 계열 (예: 다양한 구리와 아연의 비율로 이뤄진 황동)

Terminologies

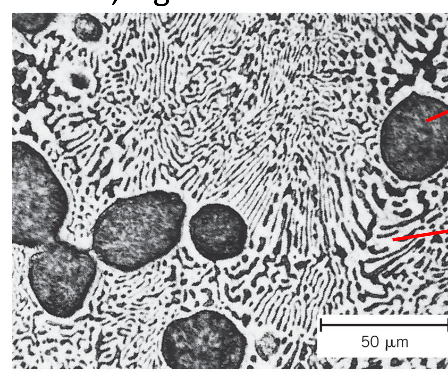
- **Alloy (합금)**
- **Phase (상):** a region of space throughout which all physical and chemical properties of a material are essentially uniform.
- **Solid Solution (고용체)**
  - Solvent (용매)
  - Solute (용질)
- **Component (구성 성분)**
- **System (계)**



Aluminum-Copper Alloy

Adapted from chapter-opening photograph, Chapter 9, Callister, Materials Science & Engineering: An Introduction, 3e.

P. 374, Fig. 11.16

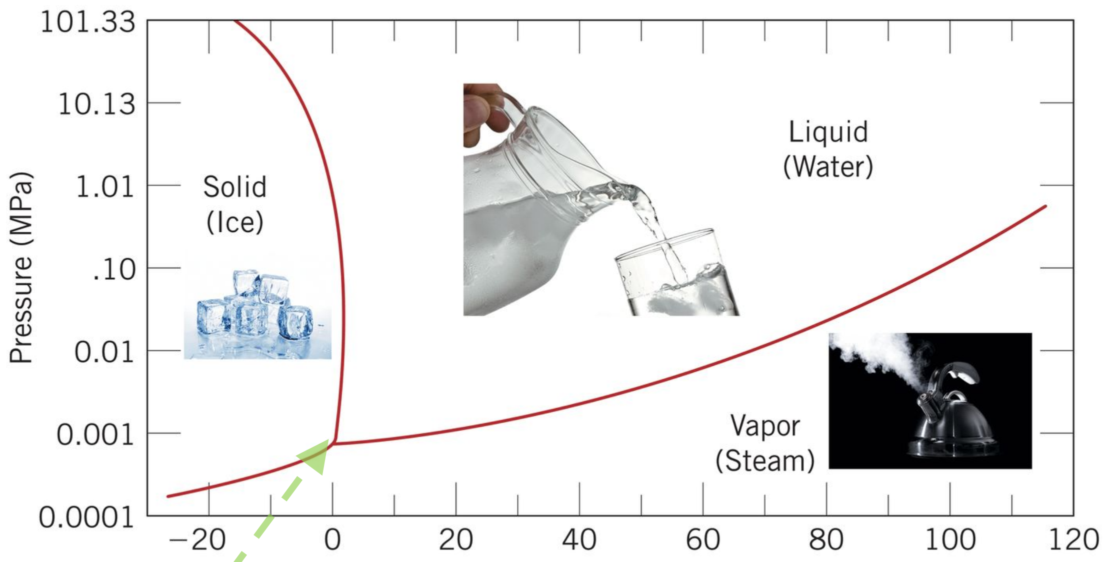


From Metals Handbook, Vol. 9, 9th edition, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.

50 wt% Sn –
50 wt% Pb alloy

예) 물의 상태도

단일 화합물로 이루어진 물은 압력(P), 온도(T)에 따라 평형상이 달라진다.



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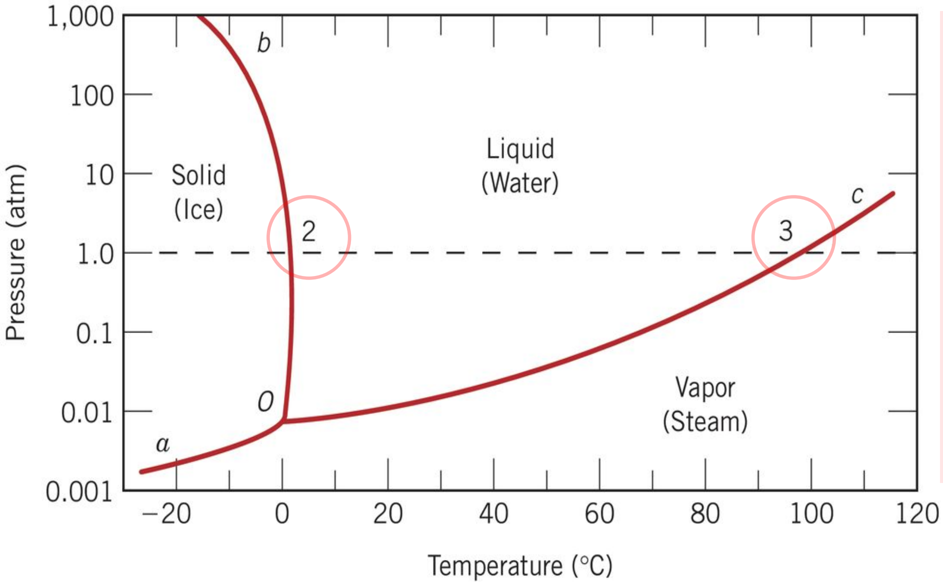
평형도 상의 경계내의 지역에서는 하나의 상이 평형을 이룬다 (안정하다). 경계선(line)위에서는 두 상이 평형을 이룬다 – 두 상이 안정한 상태로 존재.

그렇다면, 화살표가 가리키는 지점에서는 (triple point)?

단일 성분 (1원) 상태도; Unary Phase Diagram



- 대기압 조건에서 (at 1 atm), 물은 온도를 증가함에 따라, 얼음, 액체상태 물, 그리고 기체 상태 물 (수증기)로 변한다.
- 왼편의 상태도에서 2와 3 지점은 각각 녹는 점과 끓는 점을 뜻한다.

- 하나의 원소, 혹은 위와 같이 하나의 화합물 (H2O)로 만 이루어진 계 (system)의 경우에는 상태가 ‘조성’과 애초에 무관하다.
- 만약 합금이라면, 합금을 이루는 원소 (혹은 화합물) 간의 조성 관계 (섞인 비율)가 중요.

합금과 같이 두가지 (혹은 그 이상) 성분으로 이루어진 계의 경우에는?

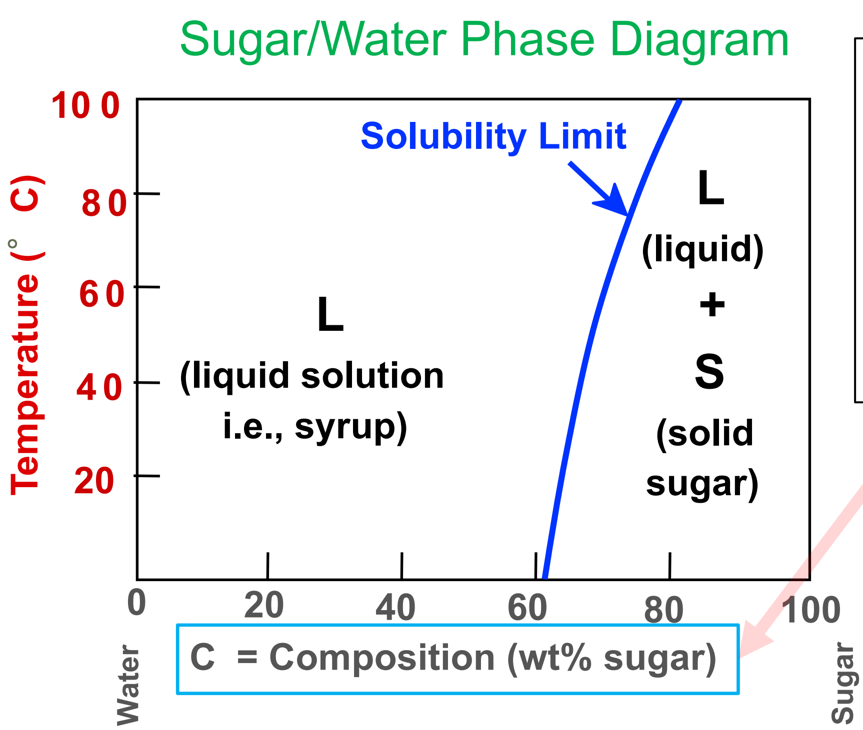
성분 원소들의 양의 비가 중요 – 게다가, ’상’의 기본 조건은 ‘균질성’을 만족하면서 최대로 섞일 수 있는 한계가 존재할 수 있다. (다음 슬라이드에서 더 다뤄보자)

Solubility limit (용해 한도)

- 설탕물의 경우
  - 설탕물 속 설탕 화합물은 균질하게 용해된 상태
  - 물: 용매 solvent;   설탕 화합물: 용질 solute
  - 균질한 섞임; 성질이 균질하게 나타남. 따라서, 설탕물은 상(phase).
- 하지만 설탕 화합물이 물속에 무한히 용해될 수는 없다. 용해 한도(solubility limit)가 존재한다.

The ratio of solute to solvent also affects the phase stability.

Composition



- 왼편의 phase diagram은 물과 설탕으로 이루어진 계의 온도 및 조성에 따라 달라지는 평형상(혹은 안정상 stable phase)을 표현한다.
- 설탕의 목에 녹는 용해 한도는 온도에 따라 변한다.

P. 351 Figure 11.1

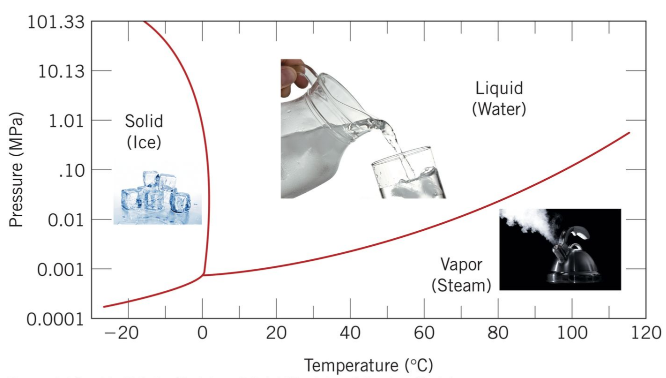
Phase diagram

- (평형) 상태도를 일컫는 다양한 용어:
  - Phase diagram
  - Equilibrium diagram
  - constitutional diagram

한 상(phase)의 안정도(degree of stability)는 다음 세 환경 변수에 영향을 받는다.
1) temperature; 2) pressure; and 3) composition

대게, 이원계(binary system)를 대상으로 상태도를 다룬다. 삼원계(tertiary system)는 여기서 다루기에 너무 복잡. 이원계 상태도는 주로, 고정된 압력하에서 온도(T)와 조성(C)에 따라 바뀌는 안정한 상들을 표현 한다.

At a fixed composition (pure water)



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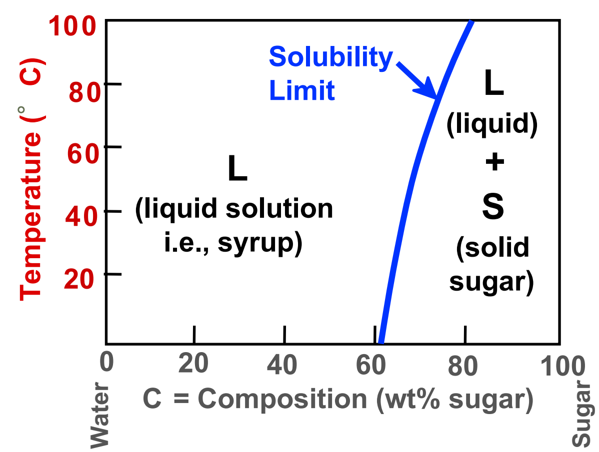
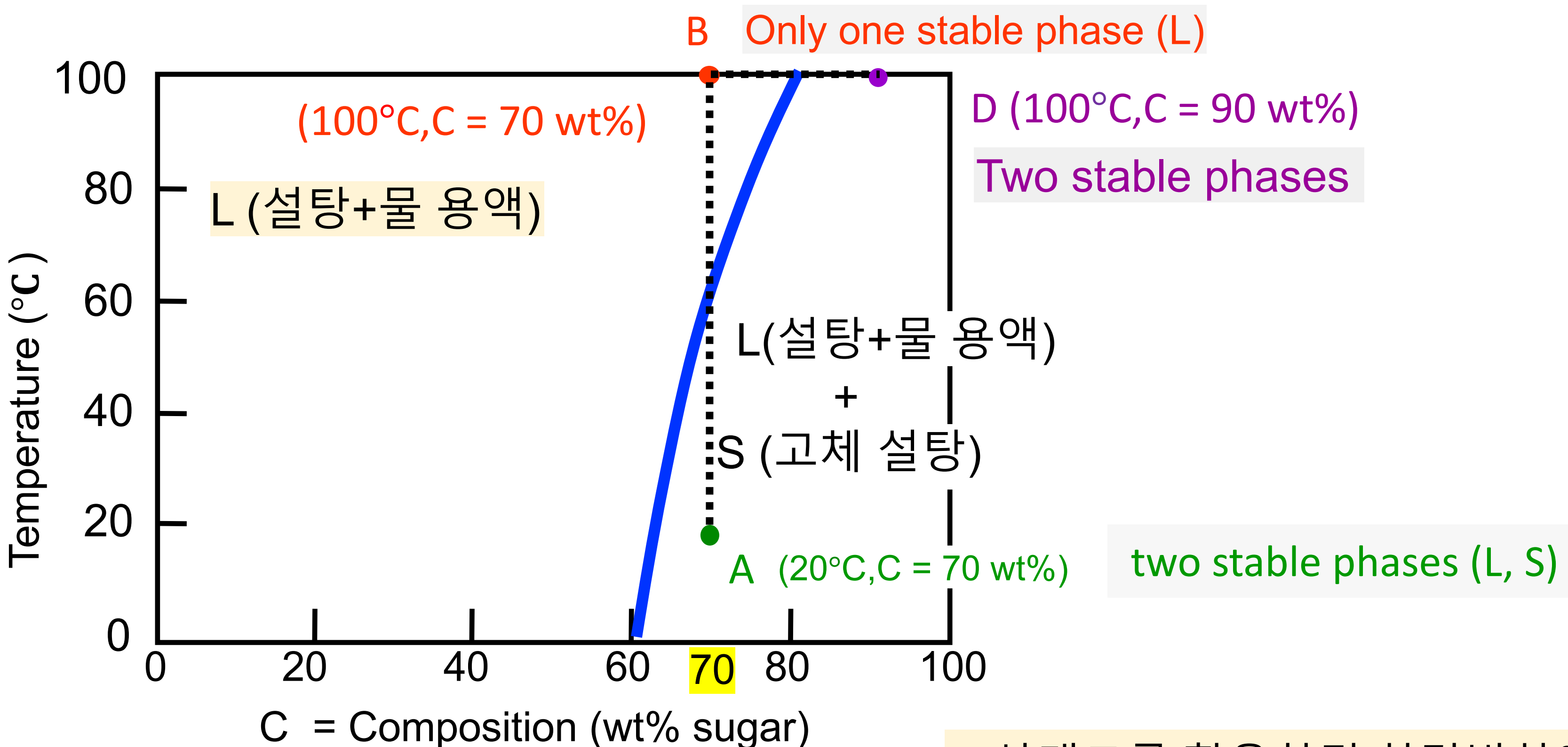
At a fixed pressure



Sugar/Water Phase Diagram

상태도의 활용 (binary system)

Water-sugar binary system



- **(A → B)** 온도 환경의 변화 → 안정상 수 변화
- **(B → C)** 조성의 변화 → 안정상 수 변화

상태도를 활용하면 환경변화에 따라 달라지는 안정상을 파악할 수 있다. (추가로 더 알 수 있는 정보들은 뒤에 따라오는 슬라이드에서 다루자)

Fig. 11.1, Callister & Rethwisch 9e.

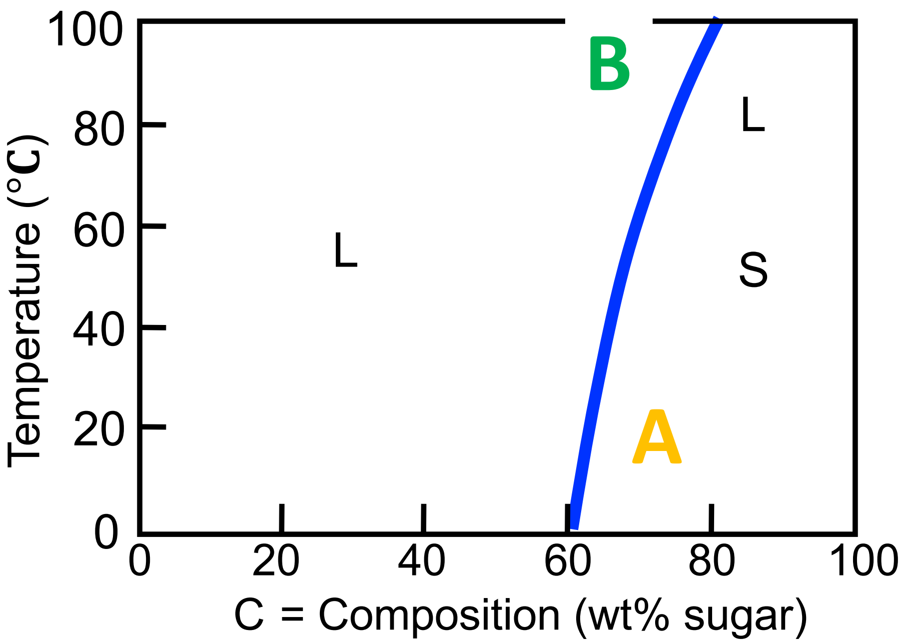
Free energy and Phase equilibrium

(상) 평형; (Phase) Equilibrium:
- 한 계가 (상)평형 상태에 놓여 있다면, 환경 (온도, 압력, 조성)이 변하지 않는 한, 시간에 따라 그 계의 성질이 변하지 않는다.
- (상)평형은 열역학(Thermodynamics)이란 학문에서 자유 에너지 (Free energy)를 사용하여 설명한다.

자유 에너지; Free energy:
- 자유 에너지는 화학적 에너지이다. 자연에서 한 계(system)는 최소의 자유 에너지를 가진 상태로 변하려 한다.
- 자유 에너지는 엔탈피 (enthalpy), 온도, 그리고 엔트로피 (entropy)에 대한 함수로 표현한다.
- 엔탈피와 엔트로피는 그 자체로 온도와 압력에 영향을 받는다.
- 따라서 열역학에서 자유 에너지는 1) 온도, 2) 압력, 그리고 3) 조성에 대한 함수로 표현한다.

상변태 (phase transformation)
- 하나의 상은 또 다른 하나(혹은 그 이상)의 상으로 변할 수 있다.
- 이는 주로 주변의 환경 조건, 즉 온도, 압력 그리고 화학조성의 변화에 의해 발생한다.
- 이러한 현상을 상변태라고 부른다.
- 예를 들어, <u>A상이 B상으로 상변태를 하고 있다</u>라고 표현하며, 열역학에서는 A상과 B상의 자유에너지의 차이를 사용하여 상변태 현상을 설명한다.
- 더 낮은 자유 에너지를 가진 상이 더욱 안정, 따라서 안정한 상(B)으로 변화해 나간다.

Free energy and Phase equilibrium: sugar-water system



A: For sugar 65wt% + water 35wt% at T=20°C:

$$G^{\text{syrup+sugar}} < G^{\text{syrup}}$$

B: For sugar 65wt% + water 35wt% at T=100°C:

$$G^{\text{syrup+sugar}} > G^{\text{syrup}}$$

If the temperature suddenly changes from A to B,

$\text{syrup} + \text{sugar} \rightarrow \text{syrup}$ (화학 반응식; chemical equation)

will occur. But this takes 'time'. The time required for this 'change' is not shown in the phase diagram.

Phase transformation and time; metastable

For metallic alloys we'll discuss, the time required for the changes between phase (phase transformation) is much slower than that of liquid system. For this reason, various microstructure will appear.

Sometimes, even if

$$G^A < G^B,$$

the phase transformation ($B \rightarrow A$) is so much slower that it does not practically occur (it may take years). In that case, phase B is called 'metastable (준평형)' under the given circumstances.

We make use of such phases in their 'metastable' conditions, which may come out from certain heat treatments. What is the metastable phase(s) that appears during the precipitate hardening? For metastable phases, in addition to temperature, pressure and composition, time is also an important factor. Non-equilibrium (metastable) phases is discussed in Chapter 12 (Fall semester).

Let's think about corrosion.

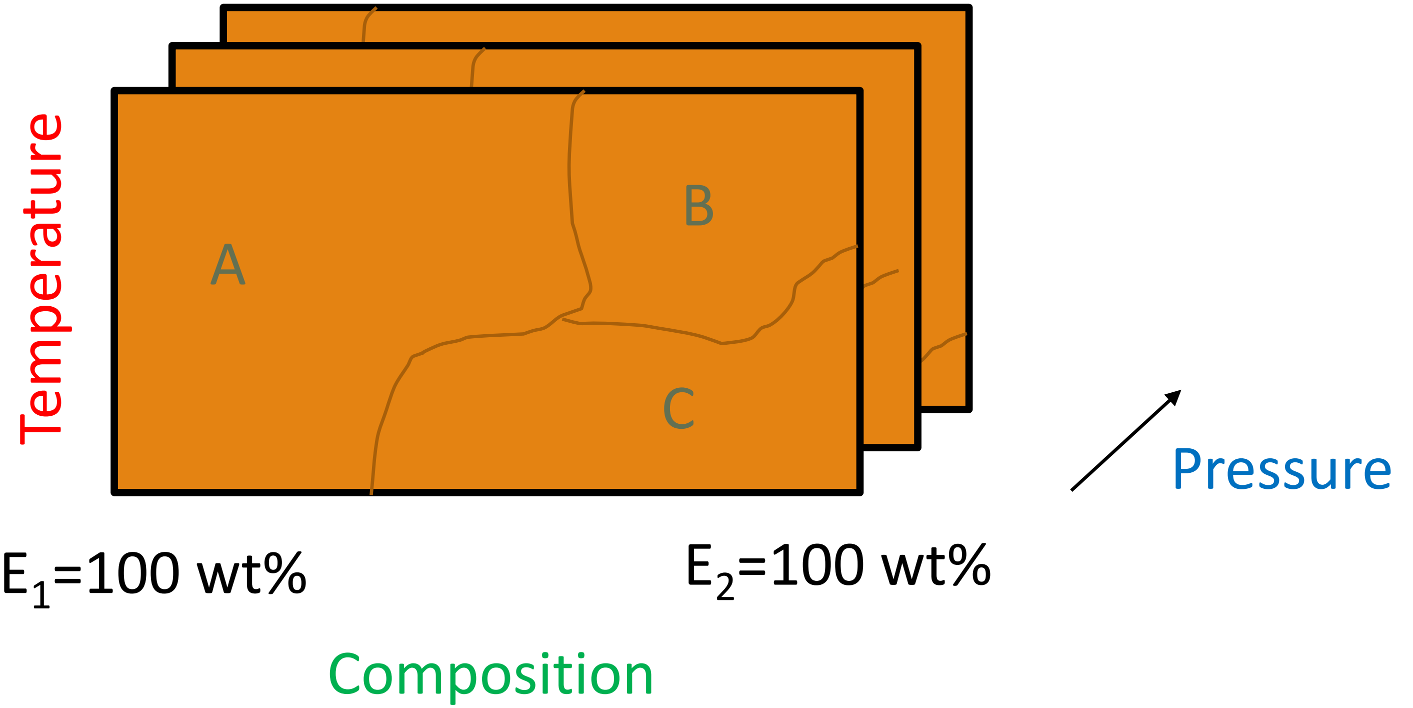
$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$$
$$Fe \rightarrow Fe^{2+} + 2e^{-1}$$
$$4Fe^{2+} + O_2 \rightarrow 4Fe^{3+} + 2O^{2-}$$
$$\vdots$$
$$Fe + H_2O + O_2 \rightarrow FeO + H_2O$$

Corrosion is a slow process. The phase in equilibrium (rust) will eventually be produced but it usually takes years. We make use of the metastable steel (or iron) phase meanwhile.

Binary phase diagram (이원 상태도)

Binary phase diagram: phase diagram for a system that consists of two elements (let's call them E_1 and E_2, respectively.)

Phase stability depends on temperature, pressure, composition.

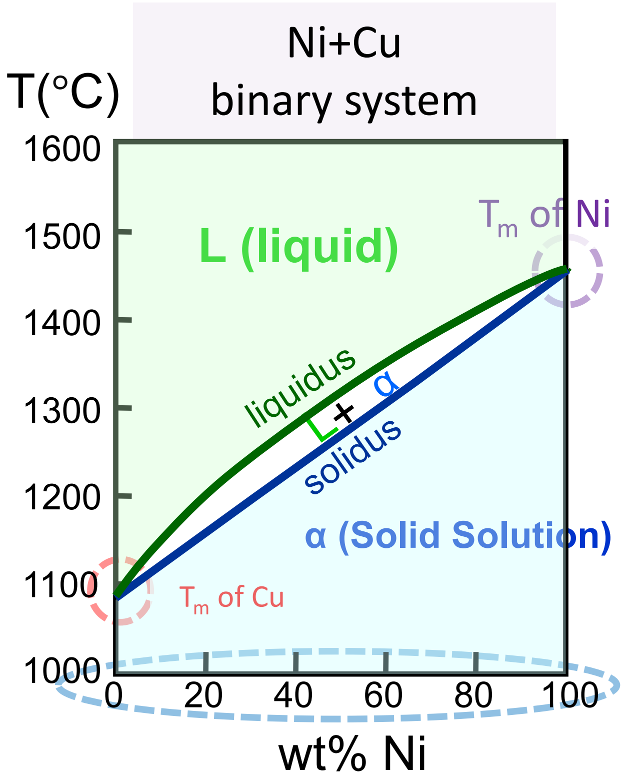


Binary phase diagram is usually refers to the one at a fixed pressure (under 1 atm = atmospheric pressure)

Cu-Ni binary isomorphous phase diagram

2원 전율고용체계; Binary isomorphous system

Isomorphous means complete solubility of one component to another



3 different regions: L, L+α, α

- L Phase: Liquidus solution; mixture of nickel and copper.
- α Phase: Solid solution in FCC structure.
  Substitutional solid solution of Ni+Cu.
- L+ α: both L and α phases exist.

Important notes:

Both Ni and Cu have FCC structure in their pure compositions:
Atomic radius, electronegativities and valence electrons are similar.
Hume-Rothery rule – conditions for solid solution. (p 159).

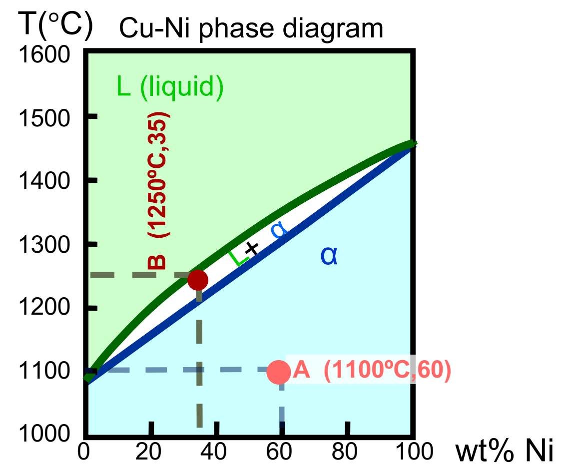
α phase (solid or liquid -solution) is possible at any composition (isomorphous)

Naming convention (nomenclature):

1. Greek letters (such as α, β, γ) are used for solid phases. Alphabet L stands for the liquid phase.
2. Boundary separating L and $\mathrm{L} + \alpha$ is termed the liquidus line (액상선)
3. Likewise, the solidus line (고상선) is the boundary between α and $\mathrm{L} + \alpha$

Information in phase diagram

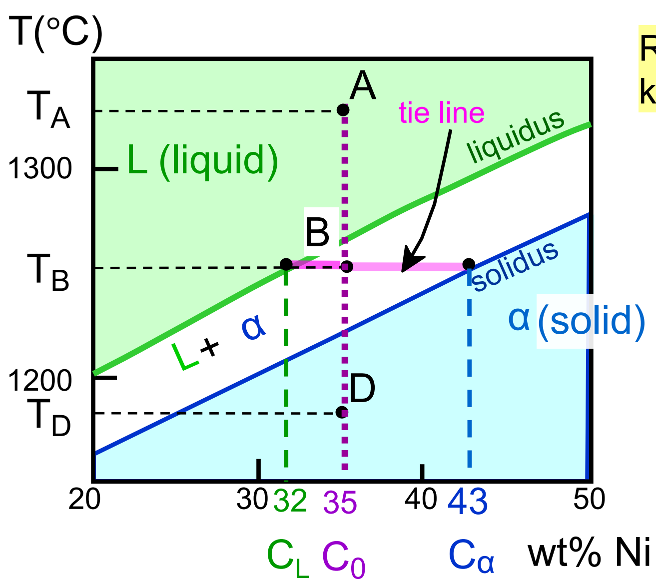
Rule 1: If we know T and C_o (좌표점 coordinates of in phase diagram), then we know which phase(s) is (are) present.



- Examples:

  A(1100°C, 60 wt% Ni): 1 phase: α

  B(1250°C, 35 wt% Ni): 2 phases: L + α



Rule 2: If we know T and C_o (좌표점 coordinates of in phase diagram), we know the composition of each phase (determination of phase composition)

For a fixed composition (C_0) for the entire system, there are cases that multiple phases may exist (such as L+α region). Each L and α phase may have different chemical compositions of Cu in Ni (or vice versa). The phase diagram can help you figure the chemical composition of each phase.

At A (T_A, C_0): L in C_0

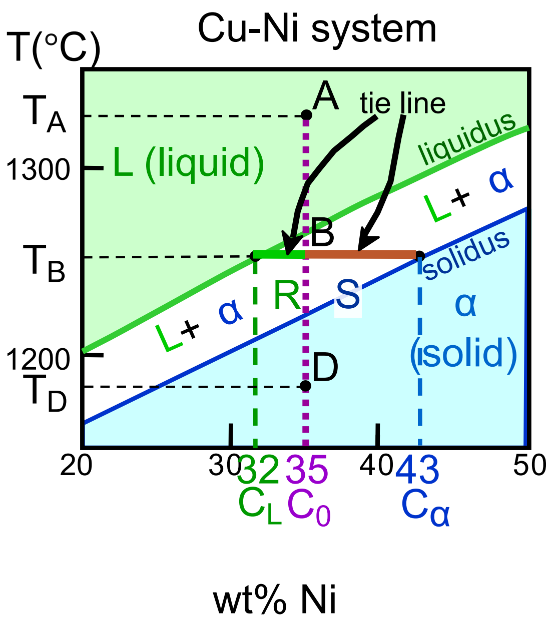
At B (T_B, C_0): L in C_L + α in C_α

At D (T_D, C_0): α in C_0

Information in phase diagram

Rule 1: If we know T and C_o (좌표점 coordinates of in phase diagram), then we know which phase(s) is (are) present.
Rule 2: If we know T and C_o (좌표점 coordinates of in phase diagram), we know the composition of each phase.

Rule 3: If we know T and C_o (좌표점 coordinates of in phase diagram), then we know the **weight fraction** of each phase (phase fraction).



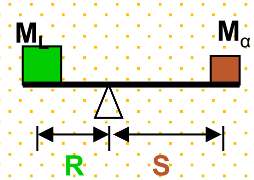
For a fixed composition (C_0) for the entire system; there are cases that multiple phases may exist (such as L+α region); Each L and α phase may exist in different amounts.

At A (T_A, C_0): Only liquid phase exist, thus $W_L = 1$, $W_\alpha = 0$
At D (T_D, C_0): Only solid (α) exist, thus $W_L = 0$, $W_\alpha = 1$
At B (T_B, C_0): Mixture of L and α; We use the lever rule (or inverse lever rule).

1. Draw the tie line
2. Indicate the chemical composite for the entire system (i.e., C_0)
3. Find the distances from (C_0, T_B) to liquidus and solidus lines, respectively. (R and S)
4. Apply the lever rule:

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} \approx 0.73 \text{ wt\%}$$

$$W_\alpha = \frac{R}{R+S} \approx 0.27 \text{ wt\%}$$



Lever rule: 지렛대 원리

* Notice that the unit; The unit used in the phase diagram is the unit of the obtained weight fraction.

Derivation of the lever rule is found in ex 11.1 P 360.

Convert wgt. fraction to vol. fraction

For a binary system with α and β solid phases, one might want to know the volume fraction rather than 'weight' fraction.

$$f_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta}$$

Can you obtain this from w_α?

Yes, but I need to know the density

v_α and v_β are volumes of α and β phase, respectively.

$$\text{Density} = \frac{\text{weight (mass)}}{\text{volume}}$$

$$f_\alpha = \frac{v_\alpha}{v_\alpha + v_\beta} = \frac{\frac{W_\alpha}{\rho_\alpha}}{\frac{W_\alpha}{\rho_\alpha} + \frac{W_\beta}{\rho_\beta}}$$

If you multiply $\rho_\alpha \rho_\beta$ on denominator (분모) and numerator (분자)

$$\boxed{f_\alpha = \frac{W_\alpha \rho_\beta}{W_\alpha \rho_\beta + W_\beta \rho_\alpha}}$$

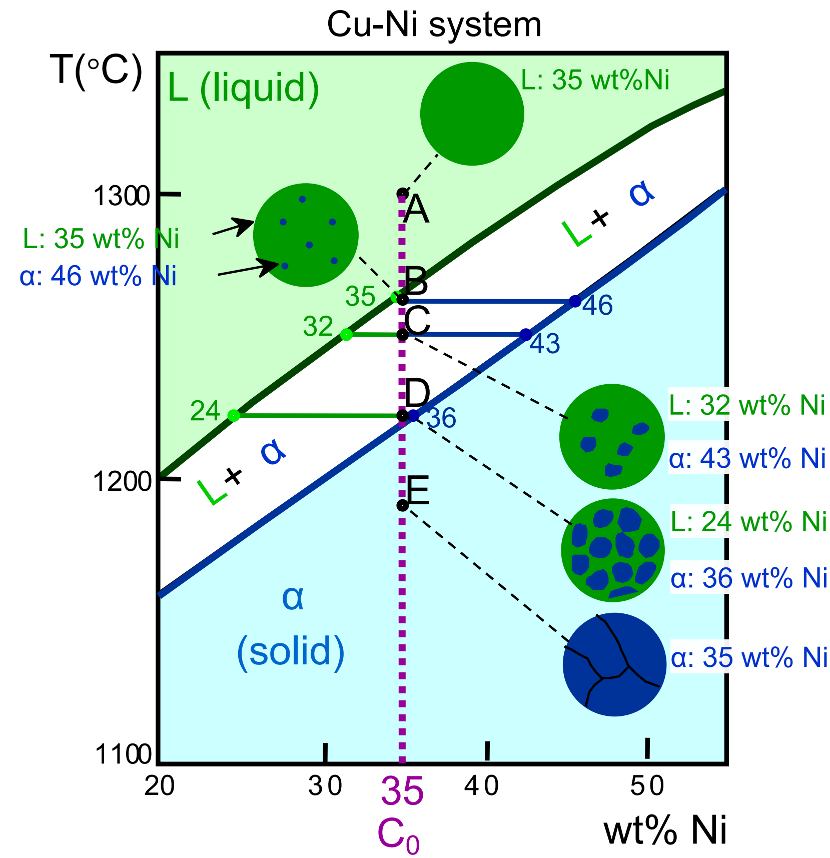
The inverse relationship of the above is:

$$W_\alpha = \frac{m_\alpha}{m_\alpha + m_\beta} = \frac{f_\alpha \rho_\alpha}{f_\alpha \rho_\alpha + f_\beta \rho_\beta}$$

Isomorphous alloy and its microstructure
(equilibrium cooling – no time required for phase transformation)

- L+α of sugar-water system, α particles will accumulate in the bottom due to gravity and density difference.
- In the absence of gravity? (Or no density difference between L and α)

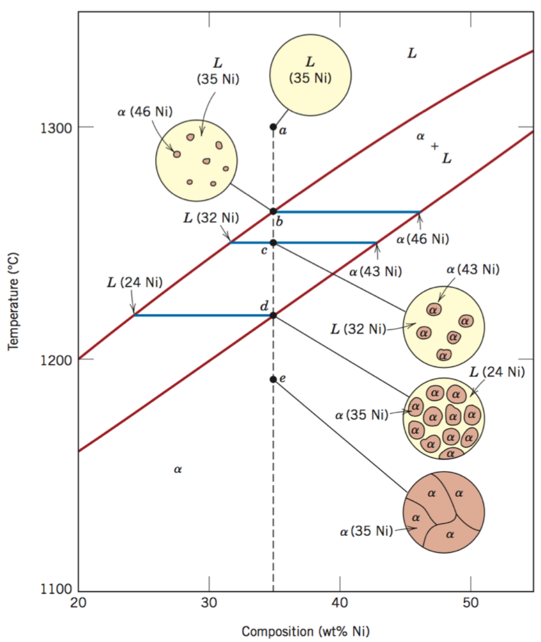
	Rule 1 (stable phase?)	Rule 2 (Comp. of each phase)	Rule 3 (Phase fraction)
A	L	$C_L = 35$ wt% Ni	$W_L = 100\%$ $W_\alpha = 0\%$
B	L+α	$C_L = 35$ wt% Ni $C_\alpha = 46$ wt% Ni	$W_L = \frac{46-35}{46-35} \times 100\%$ $W_\alpha = \frac{35-35}{46-35} \times 100\%$
C	L+α	$C_L = 32$ wt% Ni $C_\alpha = 43$ wt% Ni	$W_L = ?$ $W_\alpha = ?$
D	L+α	$C_L = 24$ wt% Ni $C_\alpha = 36$ wt% Ni	$W_L = ?$ $W_\alpha = ?$
E	α	$C_\alpha = 35$ wt% Ni	$W_L = 0\%$ $W_\alpha = 100\%$



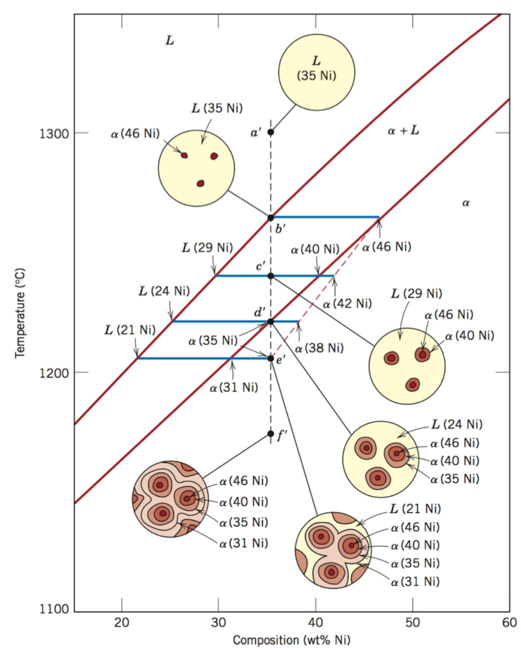
Isomorphous alloy and its microstructure
(non-equilibrium cooling – time required for phase transformation)

Phase diagram does not have information of how much time is required for phase-transformation.
The equilibrium cooling should be extremely slow to allow the transformation to start and complete – for chemical composition of solid α change, a certain flux of Ni should **diffuse** from α to the remaining L in the α+L region during cooling.

In practice, non-equilibrium cooling observed with a reasonable cooling rate.
The time required for transformation can be compensated by super-cooling or super saturation.



(a) Eq. Cooling



(b) non-eq. Cooling

Why?

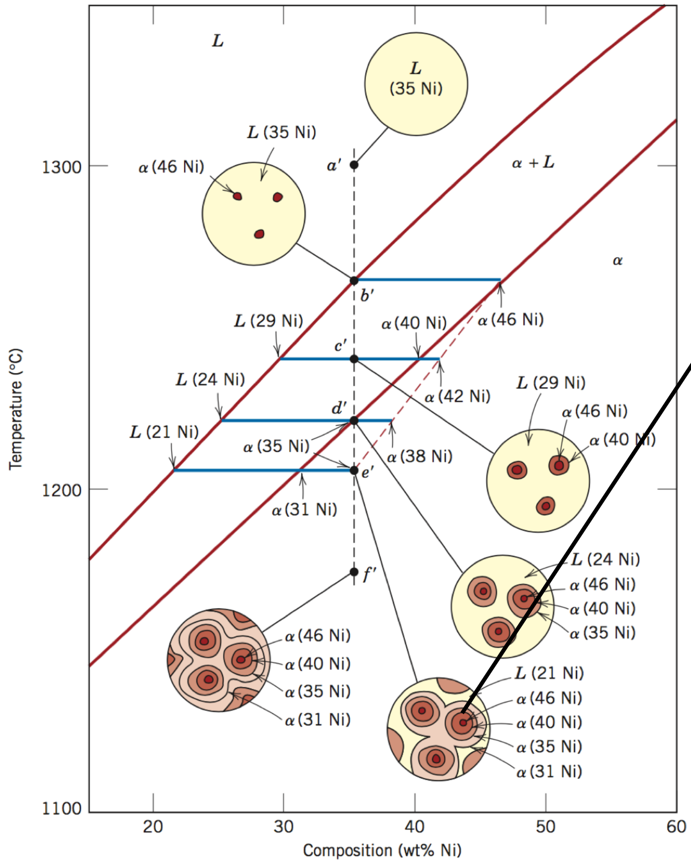
Diffusional process is involved in the transformation.

Note that diffusional process is time- and temperature-dependent.

As a result, after the cooling, the microstructure obtained by non-equilibrium cooling is not 'homogeneous' in terms of its chemical composition.

But if you let enough of time elapsed, you'll see the microstructure shown in (a).

Isomorphous alloy and its microstructure
(non-equilibrium cooling –time required for phase transformation)



Cored structure; gradient of concentration;

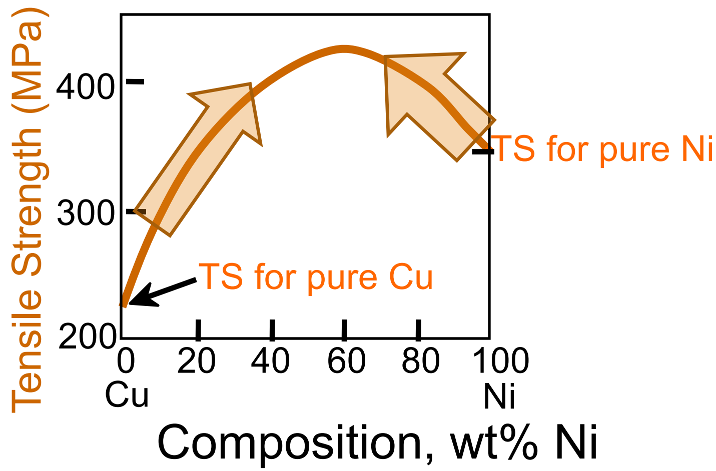
If this microstructure is unwanted, how can we make the grains homogeneous in terms of their chemical composition?

A: heat-treatment to help diffusion of Ni/Cu. This heat-treatment will produce chemically homogeneous grains.

Mechanical property of isomorphous Cu-Ni system

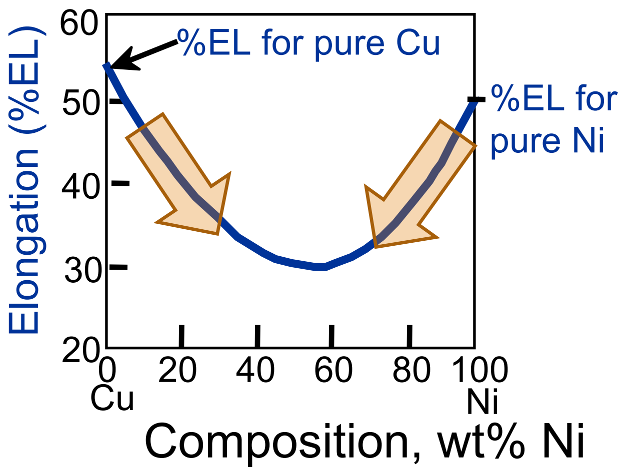
- Effect of solid solution strengthening on:

-- Tensile strength (TS)



Adapted from Fig. 11.5(a), Callister & Rethwisch 9e.

-- Ductility (%EL)



Adapted from Fig. 11.5(b), Callister & Rethwisch 9e.

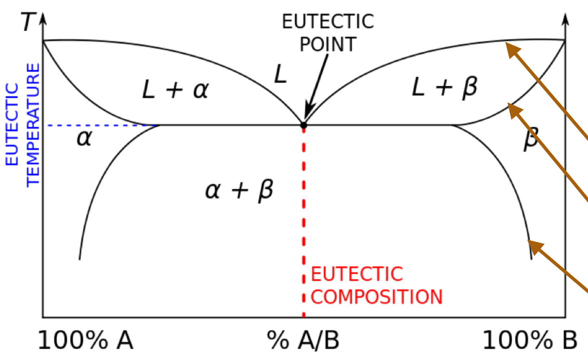
Solid-solution hardening

Ductility decreases as strengthening increases

Binary eutectic systems

- The term “Eutectic” means, easy melting.

The ‘melting’ temperature of $\alpha + \beta$ mixture is lower than that of pure α and pure β. That means, by mixing with foreign species, the melting becomes easier (eutectic).

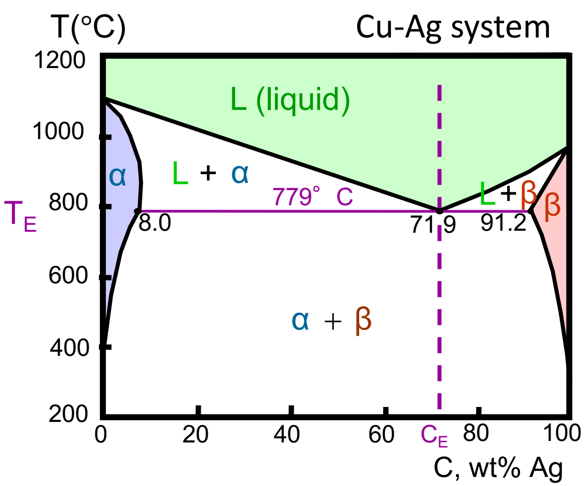


Liquidus line

Solidus line

Solvus line

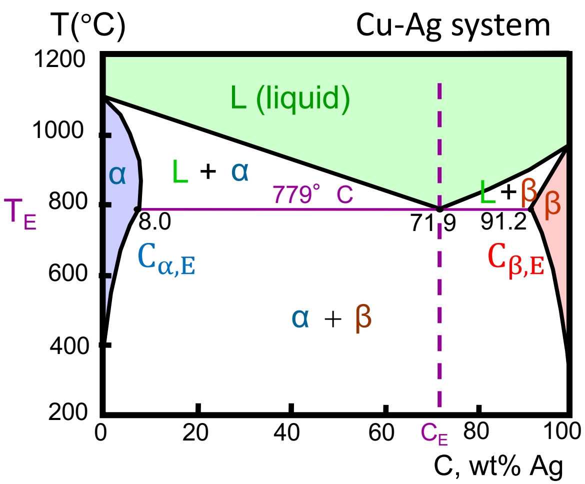
Image from Wikipedia



Characteristics of this binary eutectic systems:

1) three regions where a single phase is present (L, α solid-solution; β solid-solution)
2) α phase is a solid-solution rich in copper; silver as solute; FCC structure
3) β phase is also a solid-solution but rich in silver; copper as solute; FCC
4) Solubility of each solid-solution is reducing in $T < T_E$
5) Three regions where two phases are co-existent: $L + \alpha$; $L + \beta$; $\alpha + \beta$

Binary eutectic systems



Along the liquidus line between L and L+α, addition more solutes silver will decrease the melting temperature where α phase completely melts to L.

The same applies to the liquidus line between L and L+β; Adding more solutes (Cu) will reduce the melting temperature of β solution.

These two liquidus lines meet each other at a certain point, an invariant point of fixed C and T values (eutectic point).

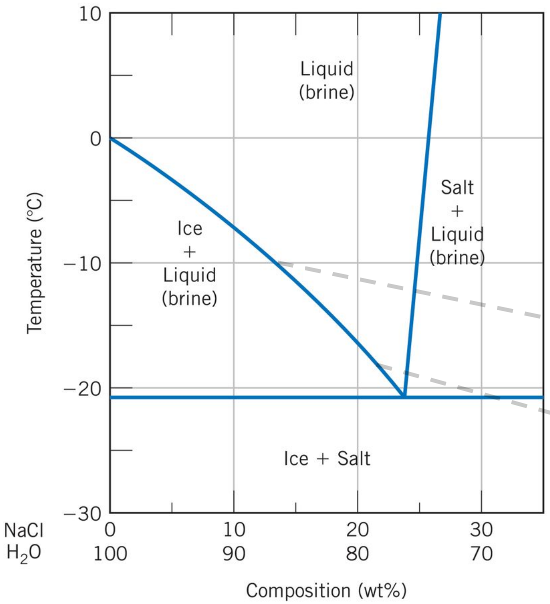
$$L\ (C_E) \underset{\text{heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \alpha(C_{\alpha,E}) + \beta(C_{\beta,E})$$

Reaction eq. at the eutectic point

C_E: Eutectic (chemical) composition
T_E: Eutectic temperature (horizontal line T_E: eutectic isotherm; 공정 등온선)
$C_{\alpha,E}$: Eutectic composition of α
$C_{\beta,E}$: Eutectic composition of β

Can you point out where (α, β and L) are co-existing? → **Invariant point (T,C are fixed)**

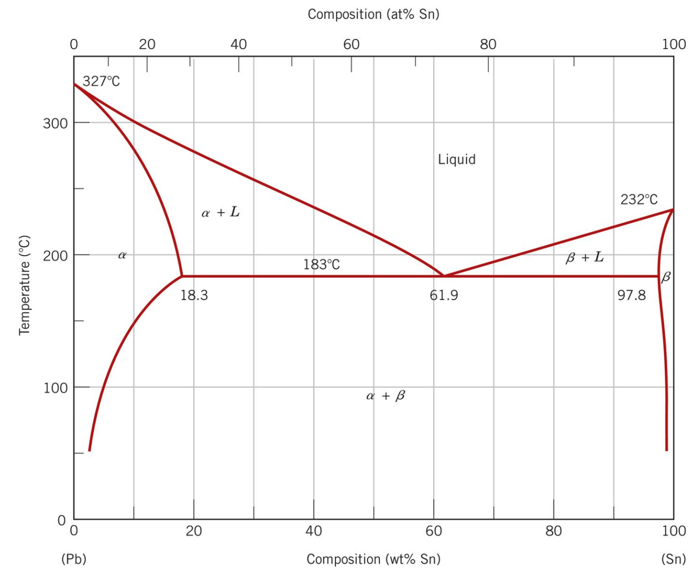
Other binary eutectic systems



얼음+소금: 어는점 내림

용해한도의 온도의존

Pb + Sn (납+주석) binary eutectic system



Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

Can you point out where is the pure ice?
Can you point out where is the pure salt?

얼음에 소금을 뿌려 녹는점을 낮춘다.

납땜 (60 wt% Sn – 40 wt% Pb) 저융점 납땜 재료로 널리 쓰인다.

*brine: 소금물

Three rules for binary eutectic system Ex1

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

  (1st rule) the phases present

  Answer: α + β

  (2nd rule) the phase compositions

  Answer: C_α = 11 wt% Sn

  C_β = 99 wt% Sn

  (3rd rule) the relative amount of each phase

  Answer:

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_0}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 0.67$$

$$W_\beta = \frac{R}{R+S} = \frac{C_0 - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 0.33$$

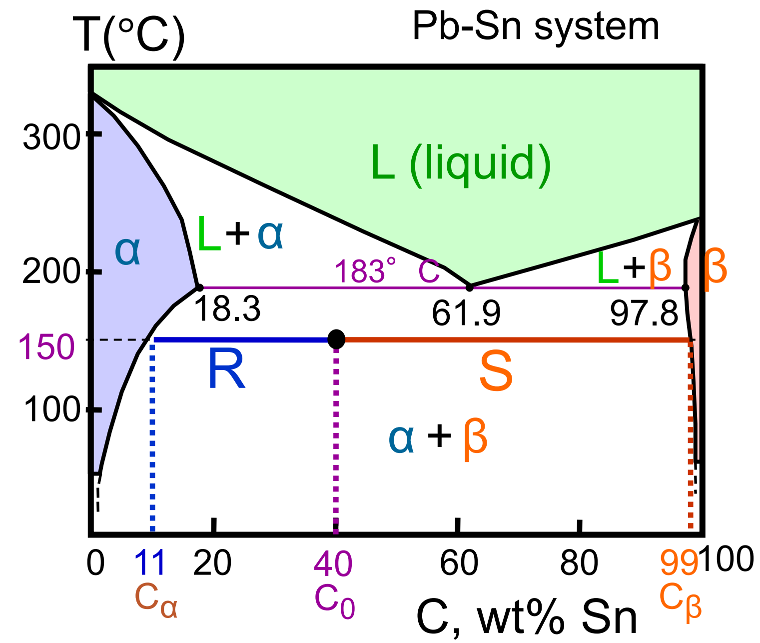


Fig. 11.7, Callister & Rethwisch 9e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Three rules for binary eutectic system Ex2

- For a 40 wt% Sn-60 wt% Pb alloy at 220° C, determine:
  (1st rule) the phases present:

  Answer: L+α

  (2nd rule) the phase compositions

  Answer: C_α = 17 wt% Sn
  C_L = 46 wt% Sn

  (3rd rule) the relative amount of each phase

  Answer:

$$W_\alpha = \frac{C_L - C_0}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 0.21$$

$$W_L = \frac{C_0 - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 0.79$$

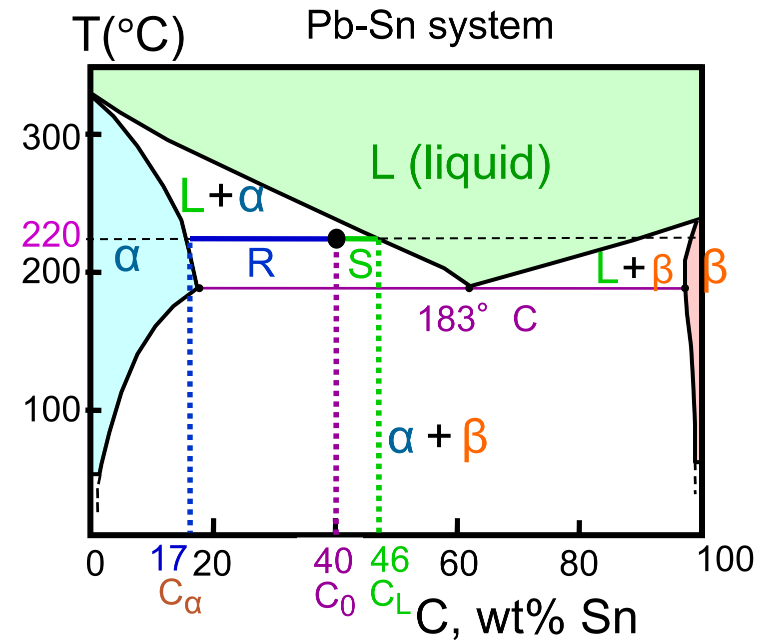
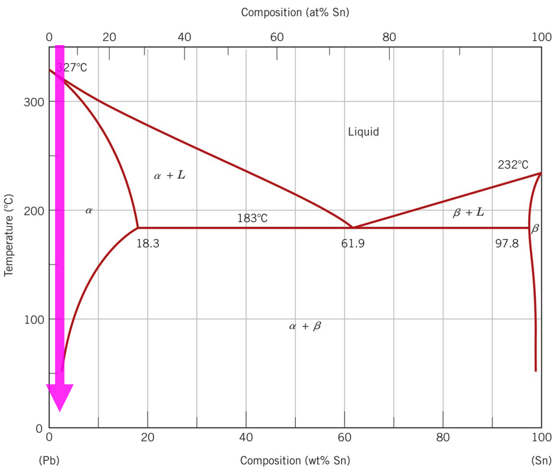


Fig. 11.7, Callister & Rethwisch 9e. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Microstructure in binary eutectic systems #1

Microstructure develops during 'cooling' from liquid state to solid. We'll examine three cooling cases that start with different compositions.

Case 1: For alloys for which $C_0 < 2$ wt% Sn
Case 2: For alloys for which 2 wt% Sn $< C_0 <$ 18.3 wt% Sn
Case 3: For alloys for which C_0 =61.9 wt% Sn= C_E
Case 4: For alloys for which 18.3 wt% Sn$< C_0 <$61.9 wt% Sn



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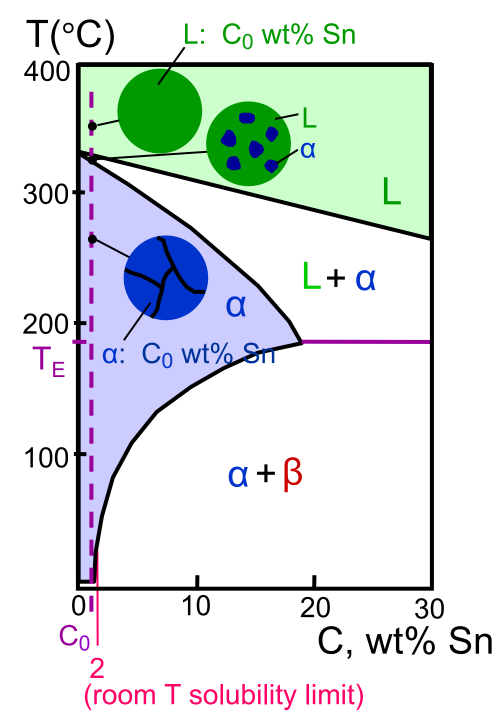


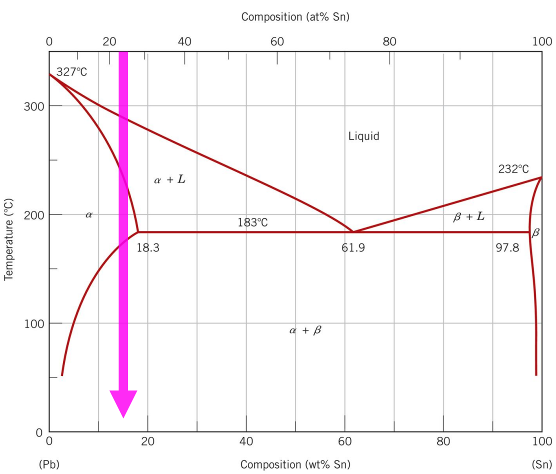
- Result: microstructure at room temperature
 -- polycrystalline with grains of α phase having composition C_0

Fig. 11.10, Callister & Rethwisch 9e.

Microstructure in binary eutectic systems #2

Microstructure develops during 'cooling' from liquid state to solid. We'll examine three cooling cases that start with different compositions.

Case 1: For alloys for which C_0 < 2 wt% Sn
Case 2: For alloys for which 2 wt% Sn < C_0 < 18.3 wt% Sn
Case 3: For alloys for which C_0 =61.9 wt% Sn= C_E
Case 4: For alloys for which 18.3 wt% Sn< C_0<61.9 wt% Sn



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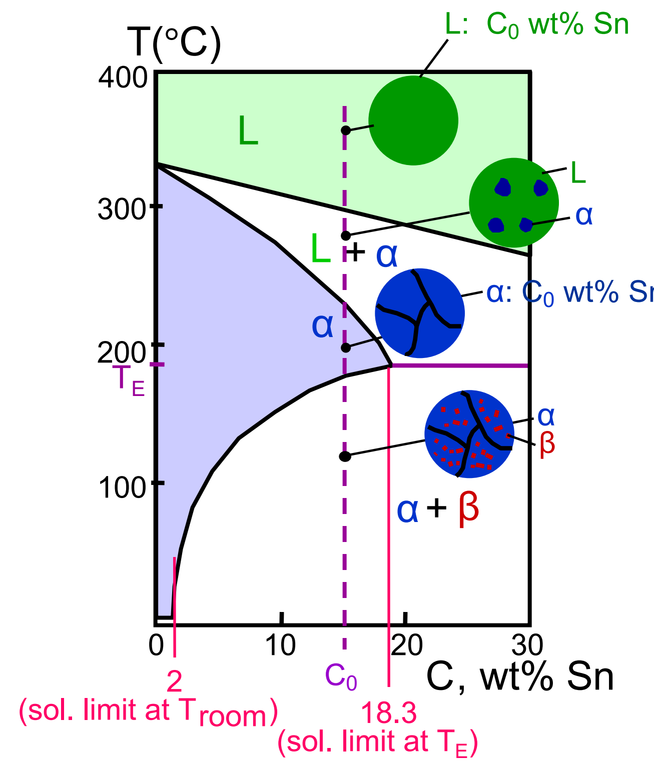
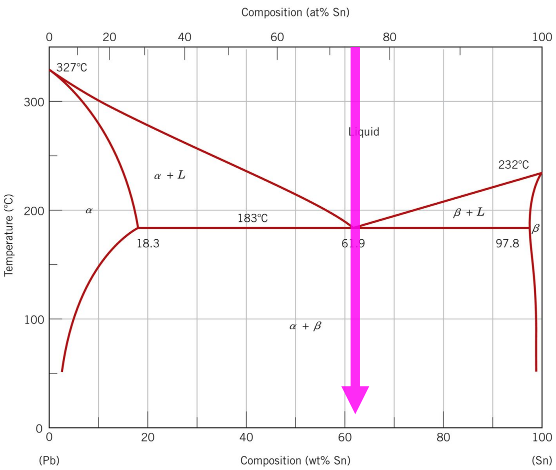


- Result: microstructure at room temperature (in α + β range)
  -- polycrystalline with α grains
  and small β-phase particles

Microstructure in binary eutectic systems #3-1

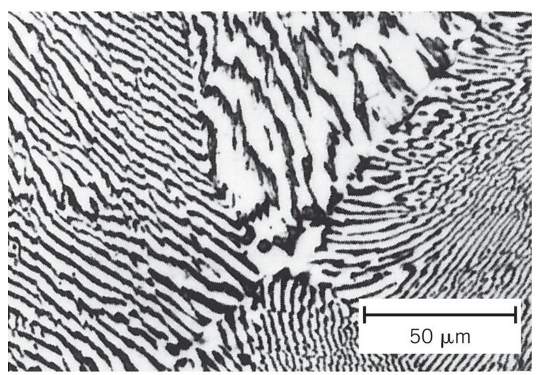
Microstructure develops during 'cooling' from liquid state to solid. We'll examine three cooling cases that start with different compositions.

Case 1: For alloys for which C_0 < 2 wt% Sn
Case 2: For alloys for which 2 wt% Sn < C_0 < 18.3 wt% Sn
Case 3: For alloys for which C_0 =61.9 wt% Sn= C_E
Case 4: For alloys for which 18.3 wt% Sn< C_0<61.9 wt% Sn

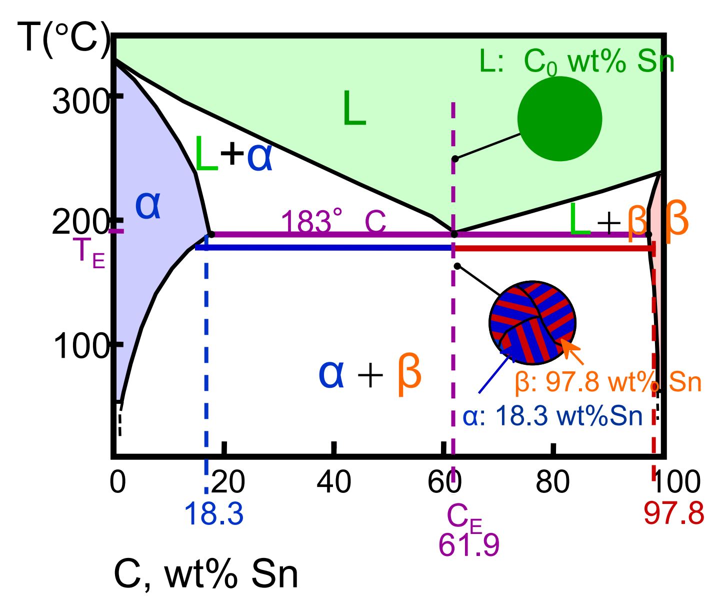


Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

- Result: Eutectic microstructure (**lamellar structure**) at room temperature (in α + β range)
  -- Alternating layers (lamellae) of α and β phases.



From Metals Handbook, 9th edition, Vol. 9, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.



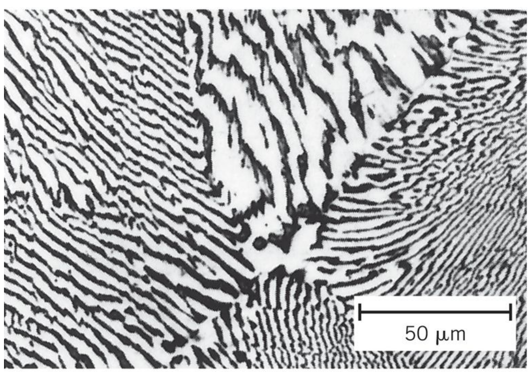
lamellar: 층상의
Lamella: 박막,박판, 주름

Microstructure in binary eutectic systems #3-2

Microstructure develops during 'cooling' from liquid state to solid. We'll examine three cooling cases that start with different compositions.

Case 1: For alloys for which $C_0 < 2$ wt% Sn
Case 2: For alloys for which 2 wt% Sn < C_0 < 18.3 wt% Sn
Case 3: For alloys for which C_0 =61.9 wt% Sn= C_E
Case 4: For alloys for which 18.3 wt% Sn< C_0<61.9 wt% Sn

- Result: Eutectic microstructure (**lamellar structure**) at room temperature (in α + β range)
  - -- polycrystalline with α grains and small β-phase particles



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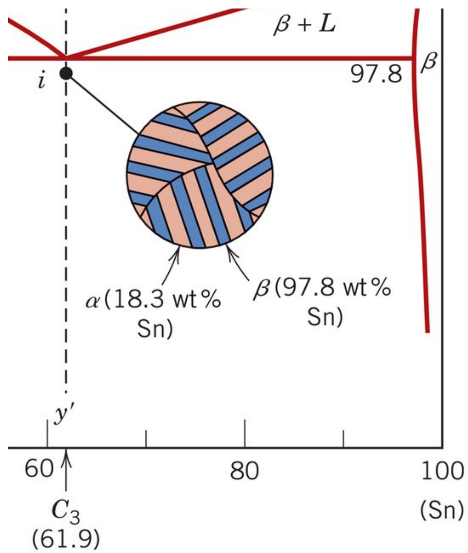
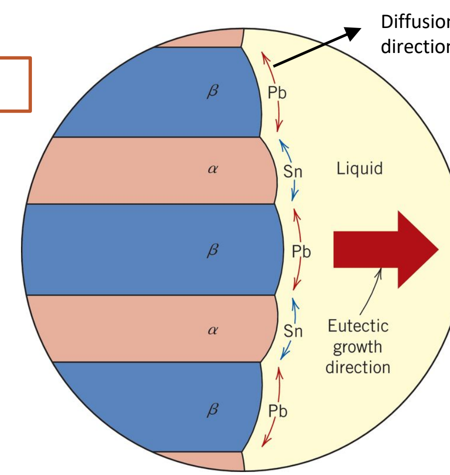


Reaction eq. at the eutectic point of Pb-Sn binary system

$$\mathrm{L}\ (61.9\ \mathrm{wt\%Sn}) \underset{\text{heating}}{\overset{\text{Cooling}}{\rightleftarrows}} \alpha(18.3\ \mathrm{wt\%Sn}) + \beta(97.8\mathrm{wt\%Sn})$$

농도 재분포 by diffusion

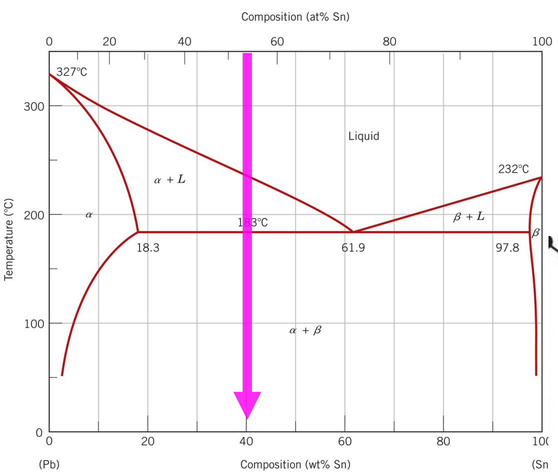
Pb 와 Sn의 확산중 '짧은' 거리 이동 가능



Microstructure in binary eutectic systems #4-1

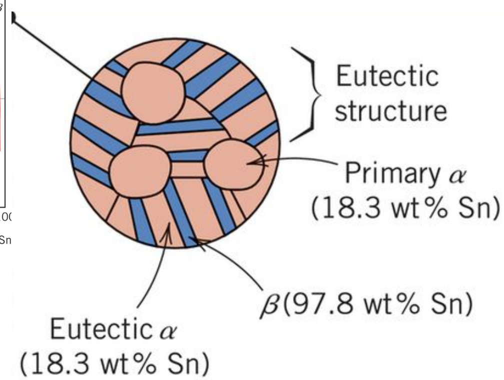
Microstructure develops during 'cooling' from liquid state to solid. We'll examine three cooling cases that start with different compositions.

Case 1: For alloys for which C_0 < 2 wt% Sn
Case 2: For alloys for which 2 wt% Sn < C_0 < 18.3 wt% Sn
Case 3: For alloys for which C_0 =61.9 wt% Sn= C_E
<u>Case 4: For alloys for which 18.3 wt% Sn< C_0<61.9 wt% Sn</u>



Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

Result: primary α phase particles + eutectic microconstituents (식별가능한 미세구성인자).



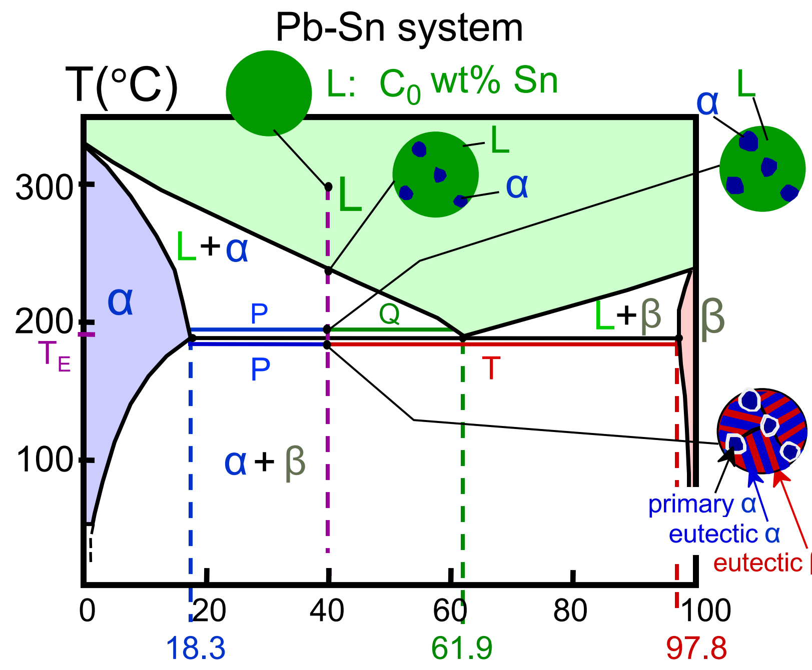
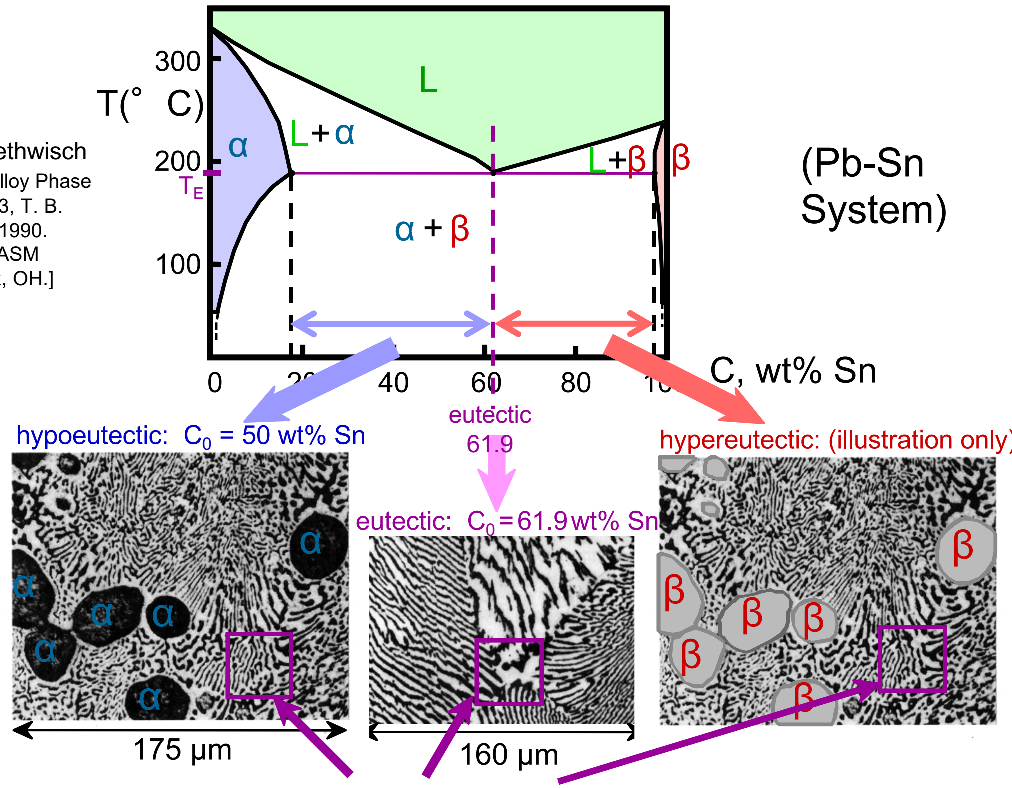


Fig. 11.15, Callister & Rethwisch 9e.

Hypoeutectic & Hypereutectic

hypo: 적은
hyper: 과도한

Fig. 11.7, Callister & Rethwisch 9e. [Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 3, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



(Pb-Sn System)

(Figs. 11.13 and 11.16 from Metals Handbook, 9th ed., Vol. 9, Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

Fig. 11.16, Callister & Rethwisch 9e.

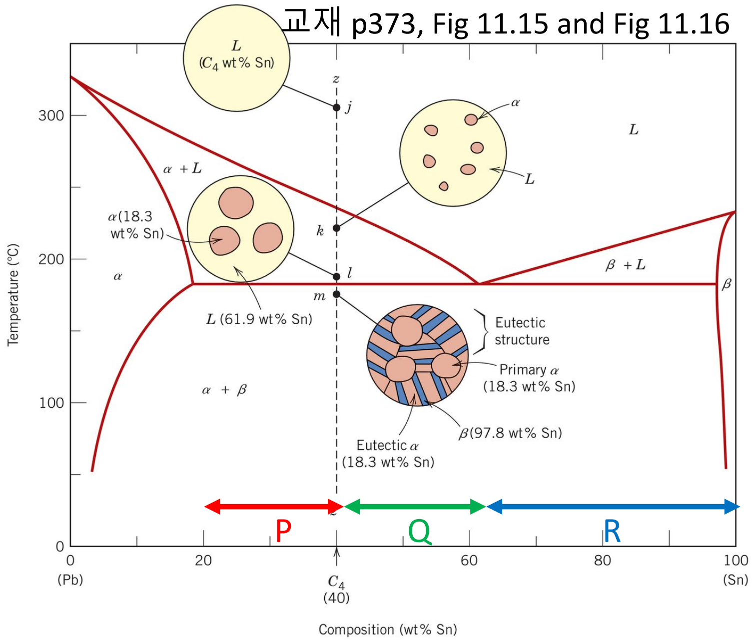
Fig. 11.13, Callister & Rethwisch 9e.

Adapted from Fig. 11.16, Callister & Rethwisch 9e. (Illustration only)

Similarly, there are
1) hypoeutectoid
2) hypereutectoid
compositions.

Microstructure in binary eutectic systems #4-2

교재 p373, Fig 11.15 and Fig 11.16



At point *m*, two types of microconstituents are observed:

1) primary α particles,
2) eutectic structure(α + β layers; lamellae)

At T just above T_E (Point l): α and L phases are present.
$W_\alpha = \frac{Q}{P+Q}$, $W_L = \frac{P}{P+Q}$

Q_1. At T just below T_E (point *m*), what are the weight fractions of primary α and lamellae structure?

$W_{\text{primary}\ \alpha}$ at point m ≈ W_α at point l

W_{eutectic} at point m ≈ W_L at point l

Q_2. At T just below T_E (point *m*), α phase exists in two separate regions: one in primary α another in eutectic structure.

$$W_{\text{primary}\ \alpha} = \frac{Q}{P+Q} \qquad W_{\text{total}\ \alpha} = \frac{Q+R}{P+Q+R}$$

Q_3. At T just below T_E (point *m*), what is the weight fraction of β?

$$W_\beta = \frac{P}{P+Q+R}$$

Q_4: What is the weight fraction of eutectic α?

$$W_{\text{eutectic}\ \alpha} = W_{\text{total}\ \alpha} - W_{\text{primary}\ \alpha}$$

Q_5. What is the chemical composition of primary α at point m?

Q_6. What is the chemical composition of eutectic α at point m?

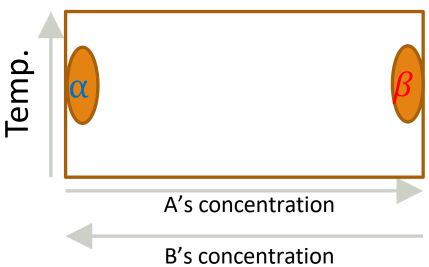
Binary systems with intermediate phase

We learned Eutectic systems with two solid solution phases

Two solid phases at the both ends of composition (at the concentration extremities; 두 고용체상이 각 상의 최대농도점 근처에 형성)

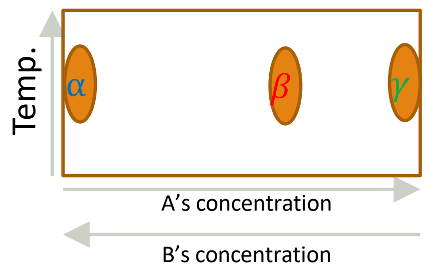
An example of binary (Zn+Cu) systems with 4 intermediate phases (Fig. 11.20)

A+B binary systems with terminal s.s.

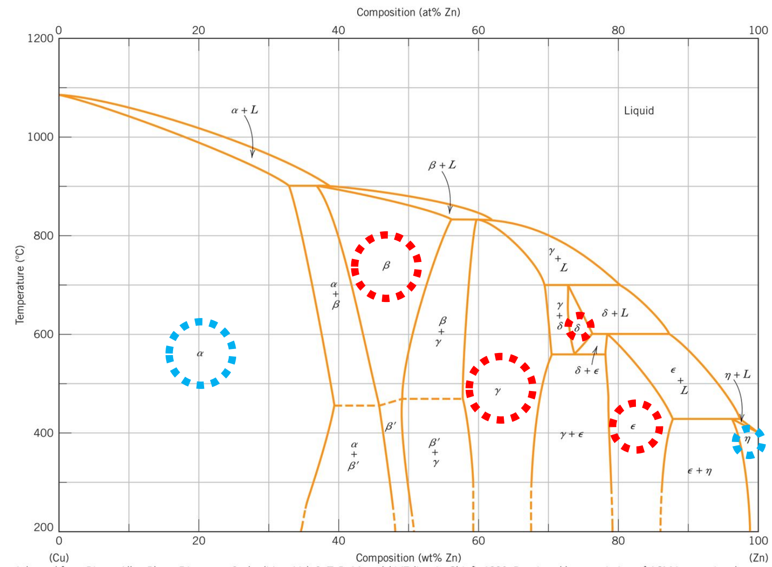


α and β phases are terminal solid solution phases.

A+B binary systems with an intermediate phase



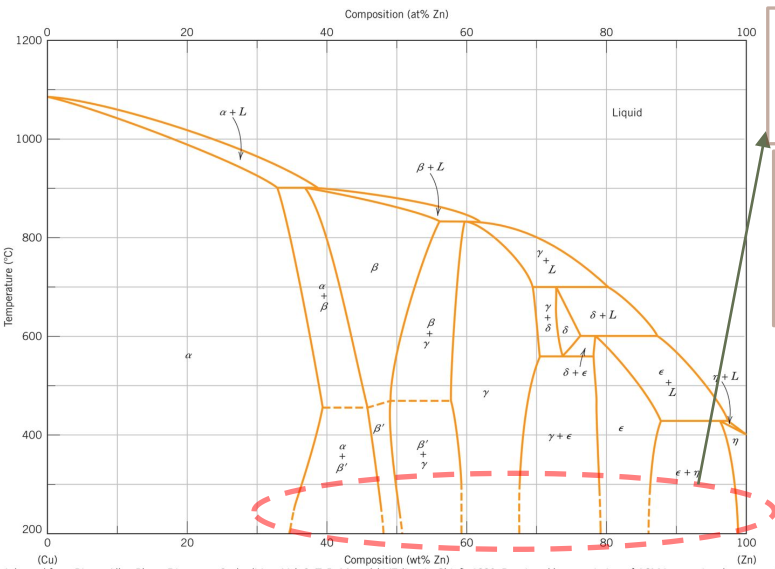
α and γ phases are terminal solid solution phases.
β phase is an 'intermediate' phase.



Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

α, η: two terminal s.s. phases
β, γ, ϵ, δ: four intermediate solid solution phases

Intermediate phases (s.s. or intermetallic compound)



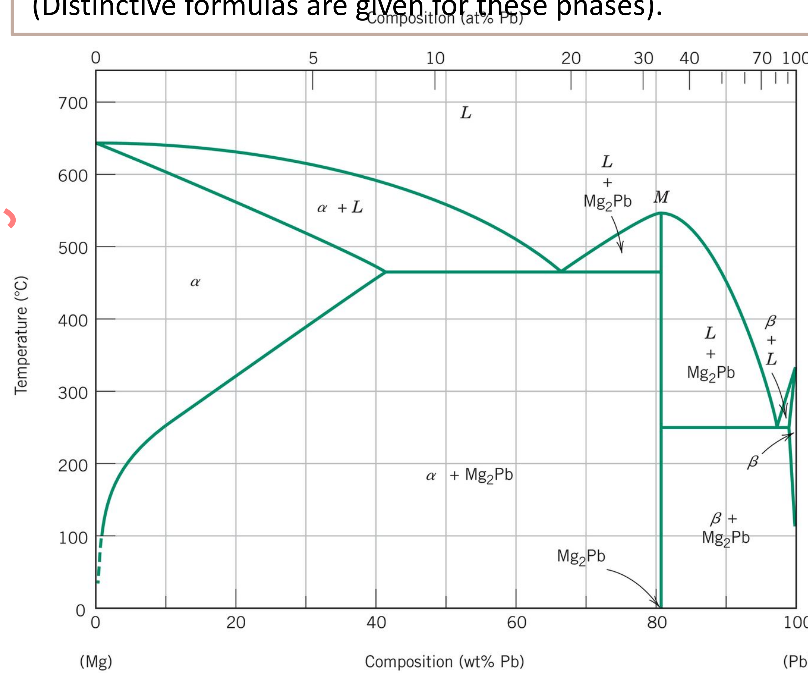
Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 2, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

상간의 경계선이 ‘점선’으로 표현: 낮은 온도에서 상평형 상태에 도달하기 위한 시간이 오래 걸려서 (diffusion) 상간의 경계선을 정확하게 실험적으로 결정하기 힘들다.

Zn-Cu systems exhibit four intermediate phases, which are all solid solutions. In certain cases (e.g., Pb-Mg binary system), intermediate phases are found to be ‘intermetallic compound, whose chemical composition should be strictly fixed (Distinctive formulas are given for these phases).

α, η: two terminal phases

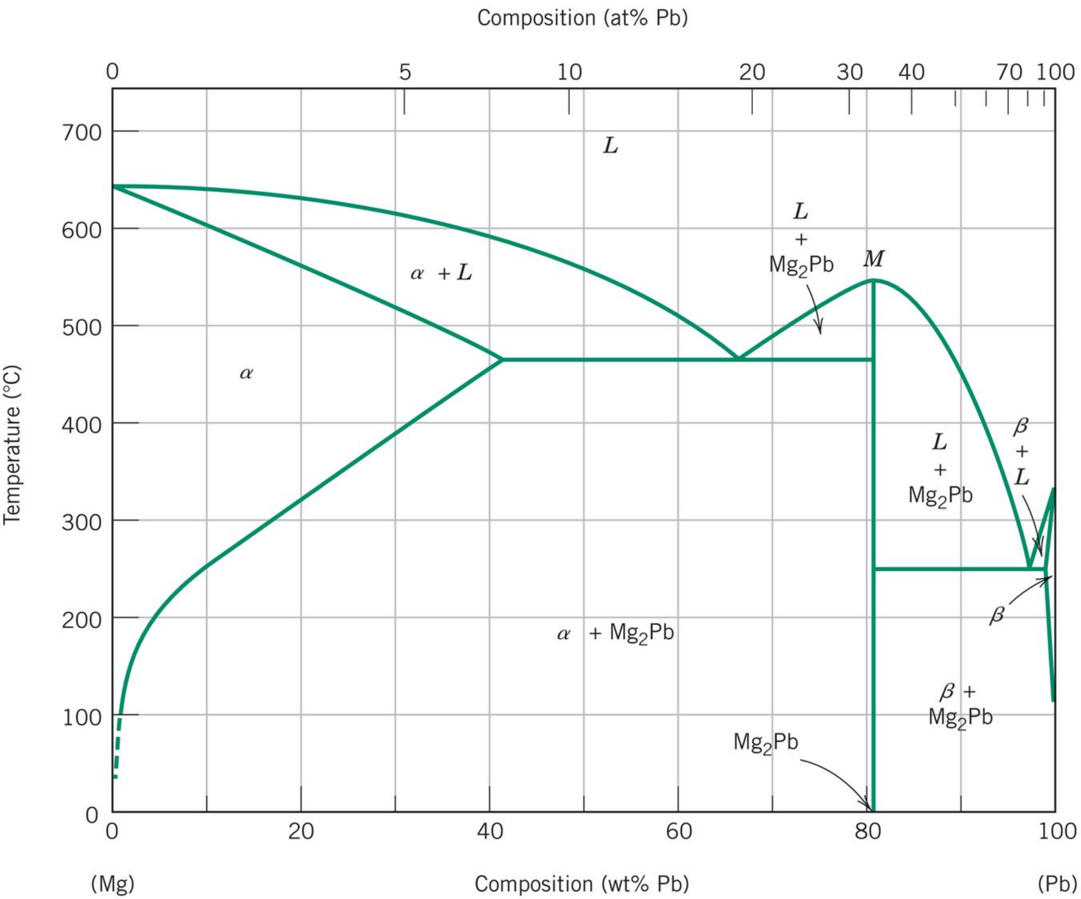
$\beta, \gamma, \epsilon, \delta$: four intermediate solid solution phases.



The domain, in which intermetallic compound phase (M, Mg_2Pb) is in equilibrium, is denoted as a ‘vertical line’.

Atomic fraction (at%) is obtained by the formula, i.e., 2:1 (66.6: 33.3)

Two eutectic diagrams in the one with an intermediate phase



Fact-check list

- Not isomorphous (not completely dissolved)
- Intermediate phase (chemical compound)
- Solubility difference between Mg and Pb: Mg can dissolve larger amount of Pb, whereas the solubility of Mg in Pb is quite limited (이 사실은 어디서 알 수 있나?)

This systems with the two terminal s.s. phases (α, β) and an intermediate chemical compound (M) can be thought of as two simple eutectic diagrams (α + M, and M + β)

Eutectic, Eutectoid and peritectic reactions

In a binary eutectic system, there is a point where L, α, and β phases may co-exist (i.e., the invariant point where T and C cannot vary)

Other invariant points?

Eutectic

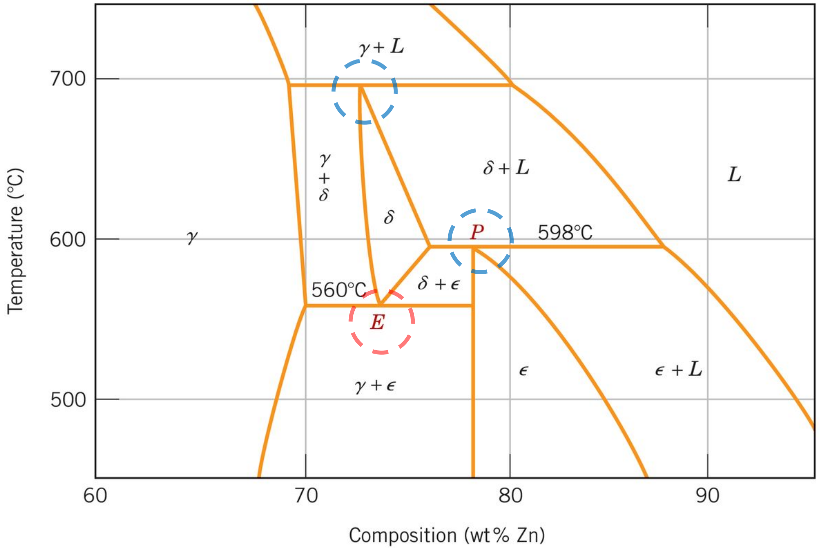
$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha + \beta$$

Eutectoid

$$S_2 \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} S_1 + S_3$$

Peritectic

$$S_1 + L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} S_2$$



How many peritectic reactions are found in Fig. 11.18?

* S,L means solid and liquid phases, respectively.

Congruent/incongruent transformation

Phase transformation divided into two classifications: one with compositional change; another without.

Phase transformation without compositional changes: congruent transformation → Allotropic transformation; meting of pure metals

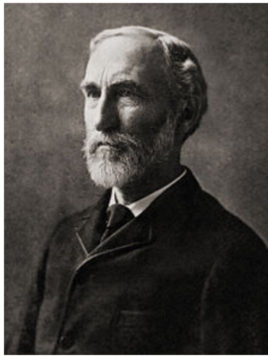
Phase transformation with compositional changes: incongruent transformation → Eutectic, eutectoid reactions; melting of alloy (isomorphous system)

Gibbs phase rule

Phase diagram is constructed by the principles of thermodynamic laws. Among many such laws, Gibbs phase rule represents a criterion for the number of phases that will co-exist within a system at equilibrium.

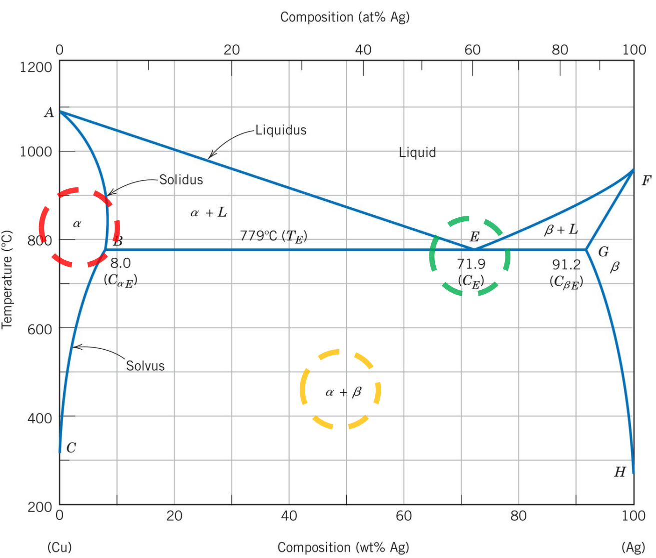
$$P + F = C + N$$

평형상태에서 함께 존재할 수 있는 상의 수를 결정해준다.



J. W. Gibbs

P: No. of phase present
F: No. of degrees of freedom (자유도의 수); No. of variables (e.g., temperature, pressure, composition)
C: No. of components in the system (elements or stable compounds; 성분 수; binary system: 2)
N: Number of noncompositional variables (composition을 제외한 변수, e.g., temperature and pressure).



Ex1: Cu-Ag binary system

1. We fixed Pressure=1 [atm]
2. Thus, N=1 (~~pressure~~, temperature)
3. Binary system (Cu-Ag). Therefore, C=2
4. P and F remain undetermined.

The Gibbs rule for this system is:
P+F=3 … (1) ;
By rearranging (1),
F=3-P … (2) for Cu-Ab binary system with Pressure=1

Let's apply **(2)** to three different domains.

α — A single phase exists:
F=3-1=2 (2 degrees of freedom)

You must define 2 variables to completely describe an alloy within this domain (in this case, comp. and temp.)

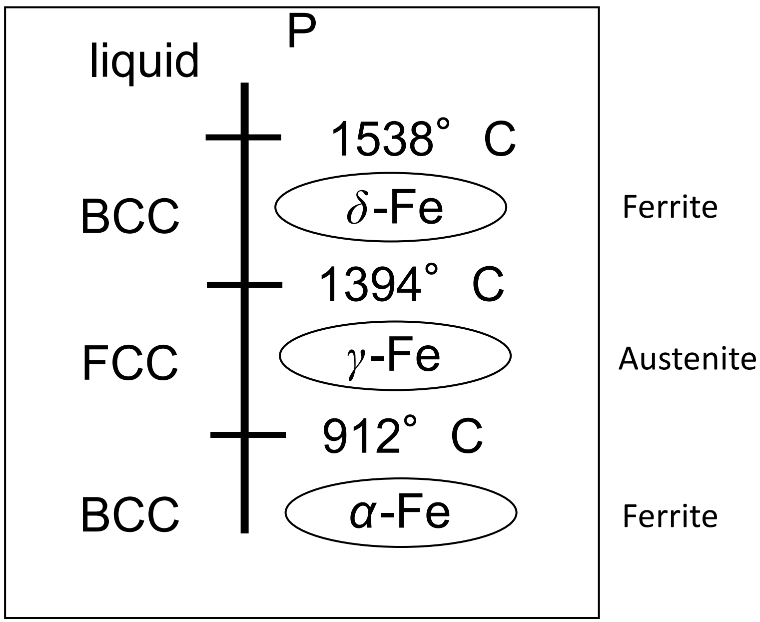
α + β — Two phases co-exist:
F=3-2=1 (1 degrees of freedom)

You must define 1 variables to completely describe an alloy within this domain (either comp. or temp).

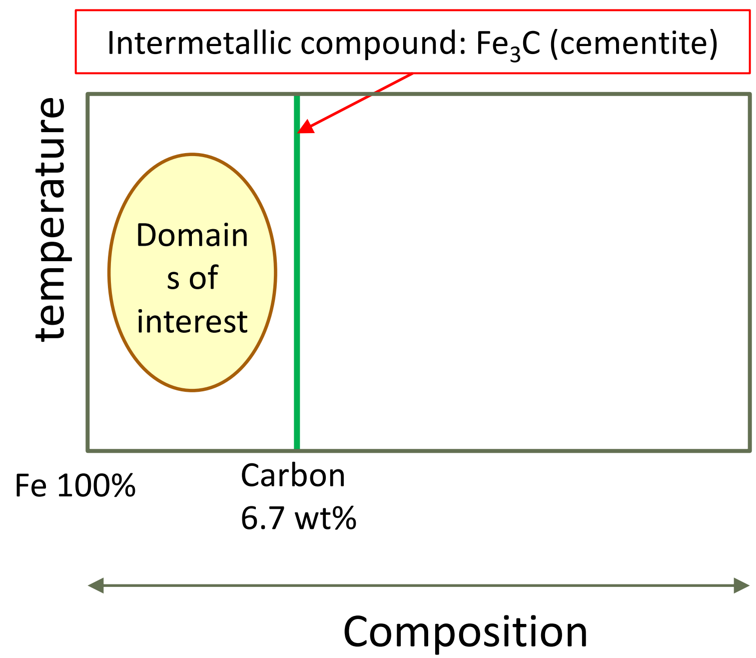
α + β + L — F=0 — Recall the 'invariant' points

Fe-C system

Pure iron system at fixed



α and γ phases can form solid solution phases by dissolving carbons (C is an interstitial atom in Fe matrix)



Remember three specific phases:

α ferrite

γ austenite

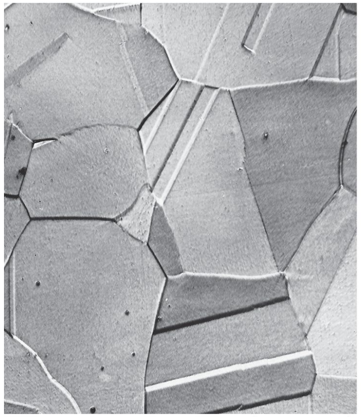
Fe_3C cementite

Properties of phases found in Fe-C system

Phases	characteristics
α ferrite	BCC, ductile, low carbon solubility (max 0.022 wt%), magnetic
γ austenite	FCC, annealing twins are often observed, high carbon solubility (max 2.14 wt%), non-magnetic
δ ferrite	Similar to α ferrite.
Fe_3C Cementite	Hard and brittle; Mixed with other phases to enhance strength; metastable; FE_3C may decompose into α iron and carbon in the form of graphite. This transformation ($FE_3C \rightarrow \alpha + \text{graphite}$) may take years.

철합금 (Ferrous alloys)의 분류:
철(pure) iron, 강 steel, 주철 cast iron: 일반적으로 carbon 의 함유량에 의해 분류된다.

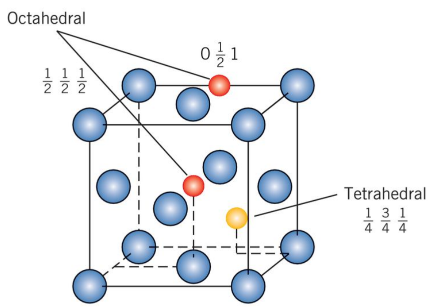
(a) 200 µm



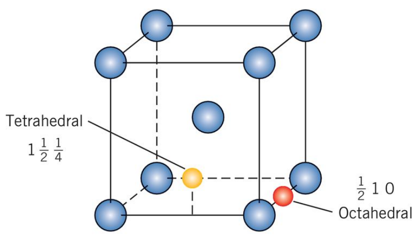
(b) 50 µm

Carbon solubility in α and γ

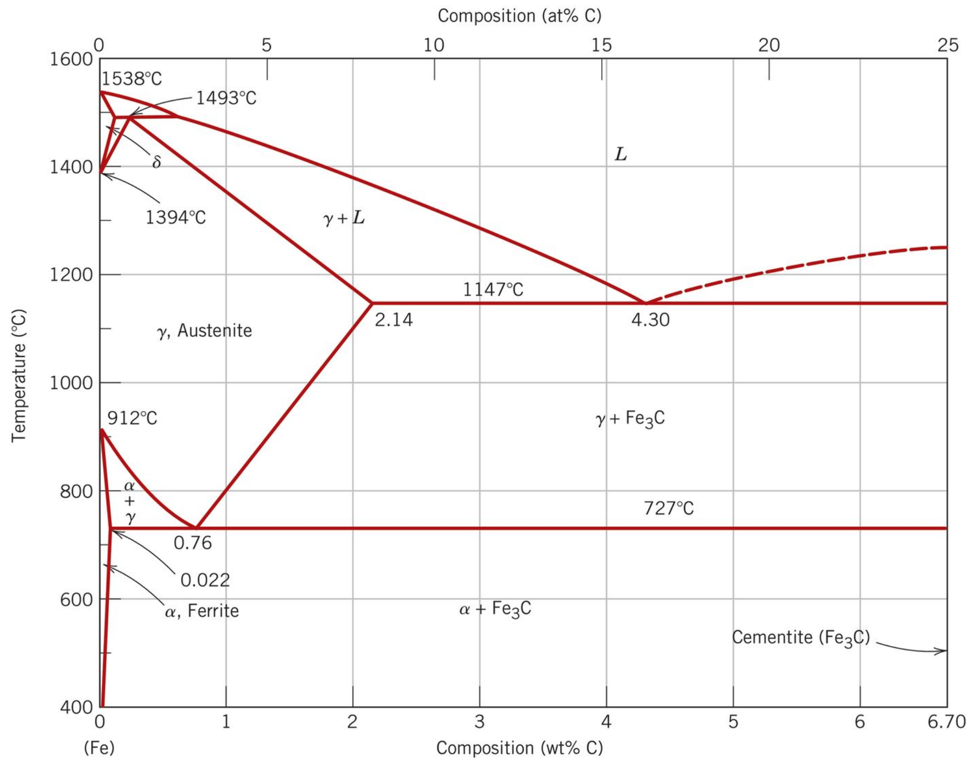
α, δ, and γ are solid solution phases of Fe-C system.
Solubility of C in Fe is mainly governed by crystal structure:
FCC can contain a lot more carbon than BCC; Octahedral sites are the primary places for carbons to reside. **The size of FCC octahedral void is much larger than that of BCC**, so that **FCC can dissolve a lot more carbons in its solid solution state.**



FCC



BCC



Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.

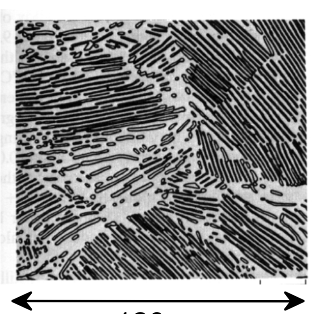
Fe-C system

- 2 important points
  - Eutectic (A):

    $L \leftrightharpoons \gamma + Fe_3C$

  - Eutectoid (B):

    $\gamma(0.76\ wt\%C) \leftrightharpoons \alpha(0.022) + Fe_3C(6.7)$



Result: Pearlite = alternating layers of α and Fe_3C phases (lamellar structure)

Fig. 11.26, Callister & Rethwisch 9e.
(From Metals Handbook, Vol. 9, 9th ed., Metallography and Microstructures, 1985. Reproduced by permission of ASM International, Materials Park, OH.)

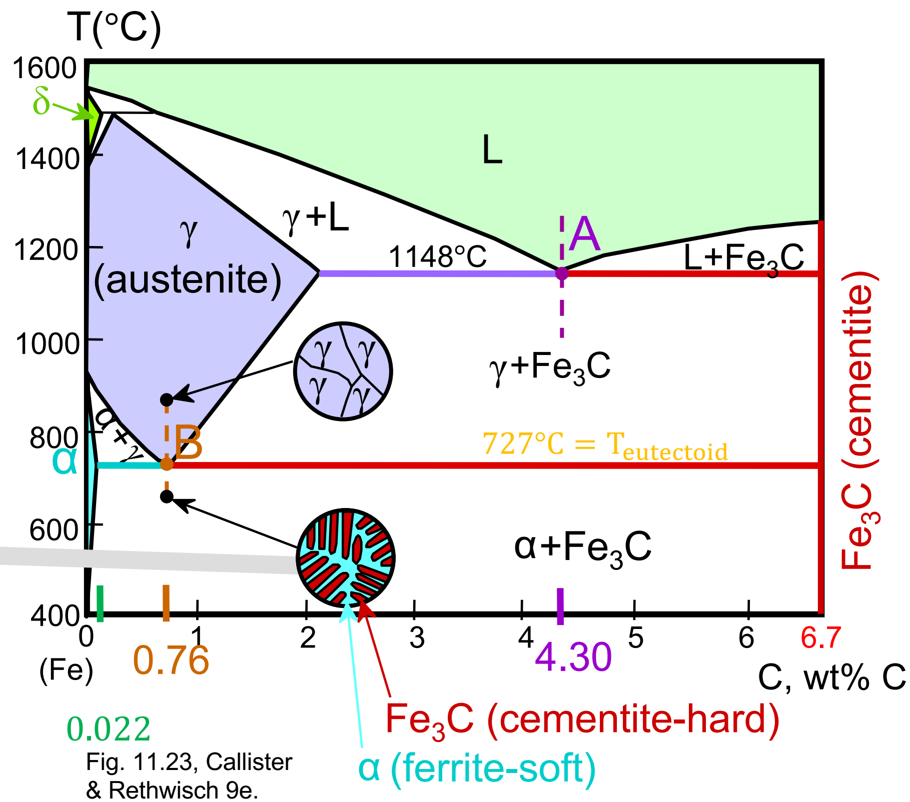
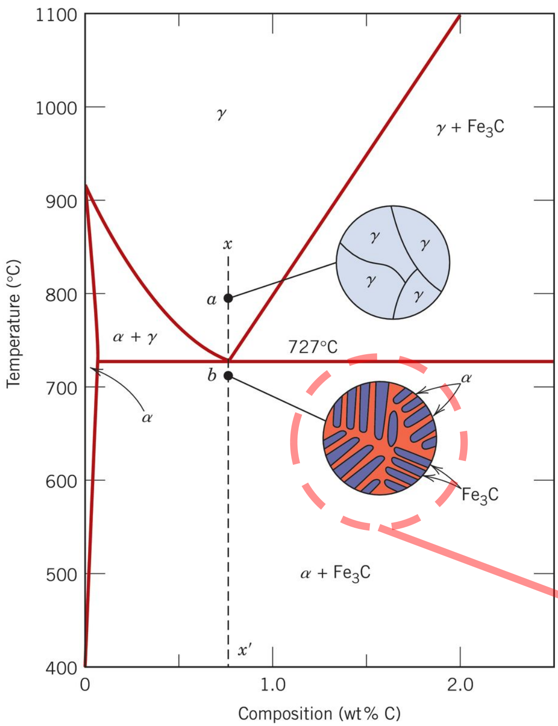
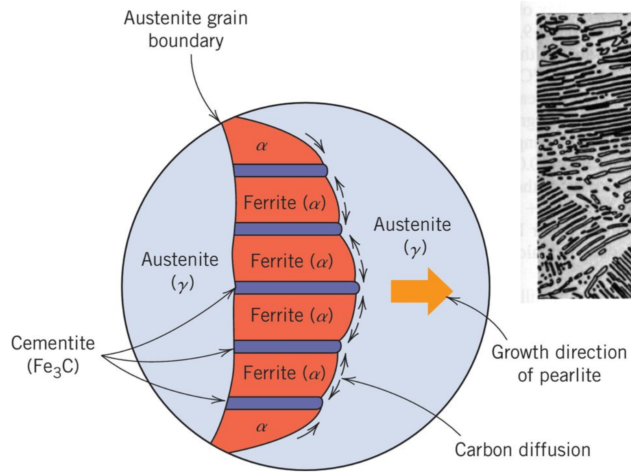


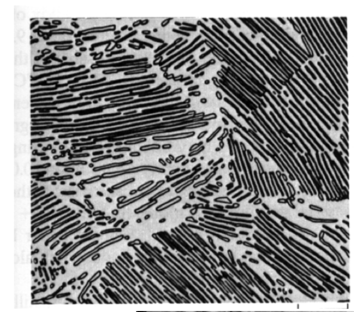
Fig. 11.23, Callister & Rethwisch 9e.
[Adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

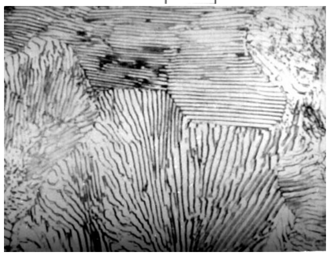
Microstructure of eutectoid steel (pearlite)

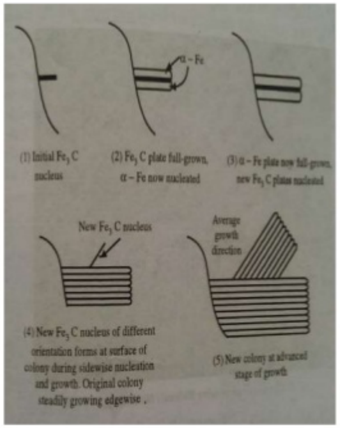




pearlite (진주조개 모양)



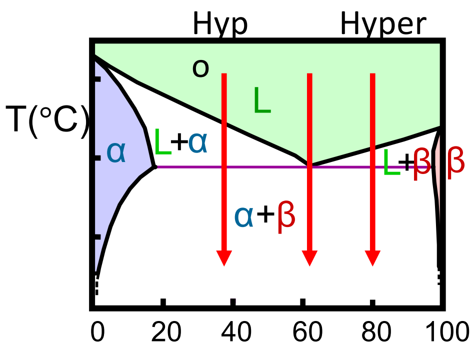


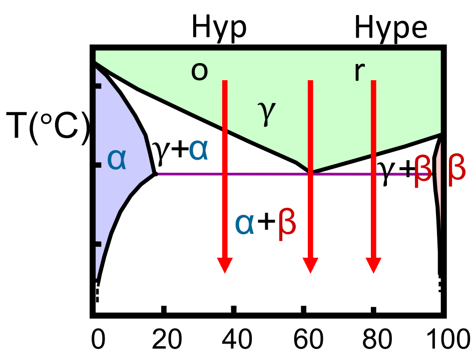


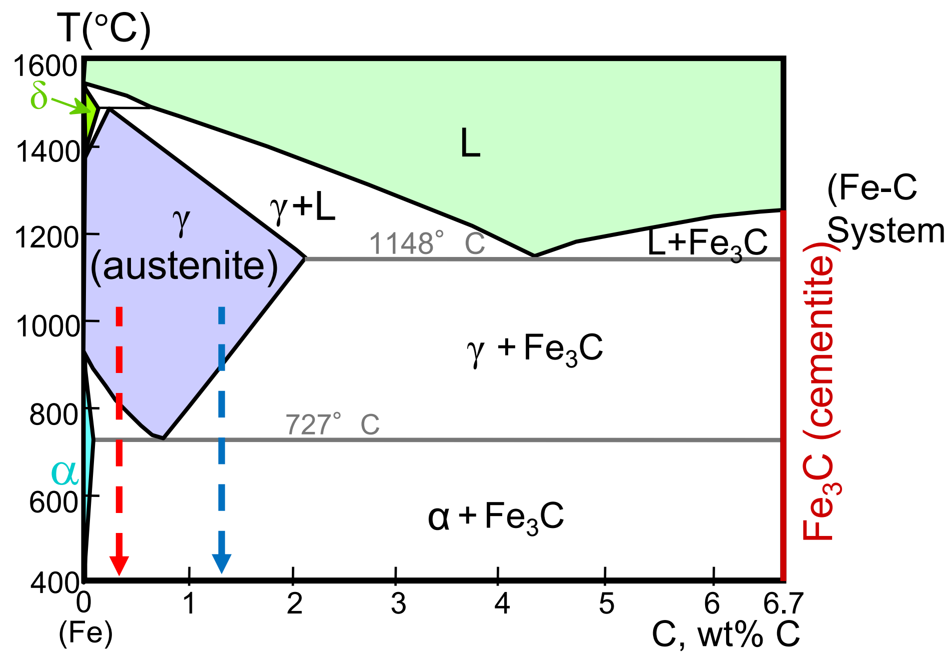
Nucleation and growth of pearlite colonies [Source: V.D. Kodgoire, S.V. Kodgire, 2010]

The eutectoid steel exhibits a structure similar to the eutectic structure discussed earlier, that is a lamellar structure consisting of (α ferrite and Fe_3C cementite). The thickness ratio of layers found in eutectoid steel is 8(α):1(Fe_3C).

Hypo and Hyper eutectoids







Hypoeutectoid

Hypereutectoi
d

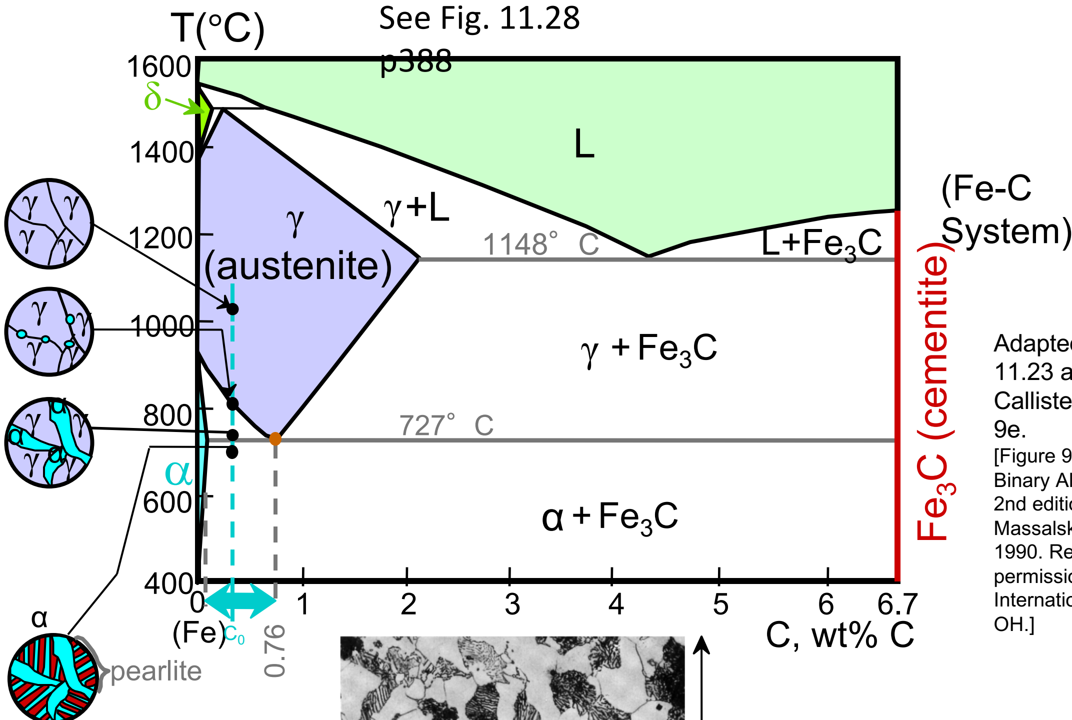
Hypoeutectoid Steel (Microstructure)

We start with a fully austenitic polycrystal

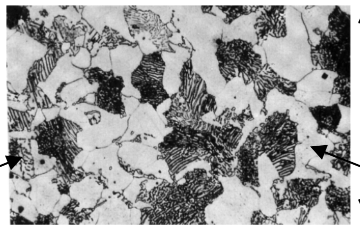
α phase nucleates in the boundaries of γ grains (why g.b. ???)

α particles keep growing along the g.b. of γ.

The remaining γ transforms to pearlite.



Adapted from Figs. 11.23 and 11.28, Callister & Rethwisch 9e.
[Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

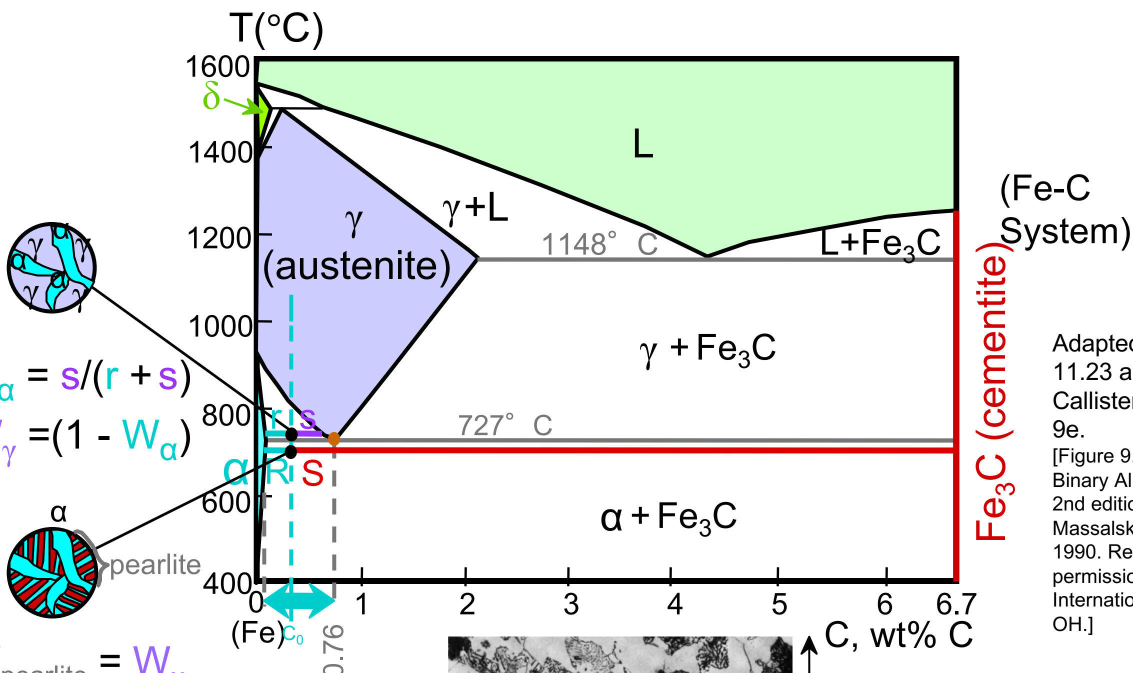


Adapted from Fig. 11.29, Callister & Rethwisch 9e.
(Photomicrograph courtesy of Republic Steel Corporation.)

There are two forms of α phase found in Hypoeutectoid steel:

1) α layer in pearlite
2) proeutectoid α ferrite

Hypoeutectoid Steel (Rule III)



$W_\alpha = s/(r + s)$

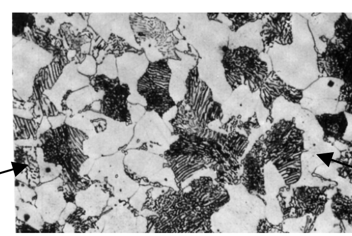
$W_\gamma = (1 - W_\alpha)$

$W_{pearlite} = W_\gamma$

$W_{pro.\alpha} = S/(R + S)$

$W_{Fe_3C} = (1 - W_{pro.\alpha})$

Adapted from Figs. 11.23 and 11.28, Callister & Rethwisch 9e.
[Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



100 µm

Hypoeutectoid steel

pearlite

proeutectoid ferrite

Adapted from Fig. 11.29, Callister & Rethwisch 9e.
(Photomicrograph courtesy of Republic Steel Corporation.)

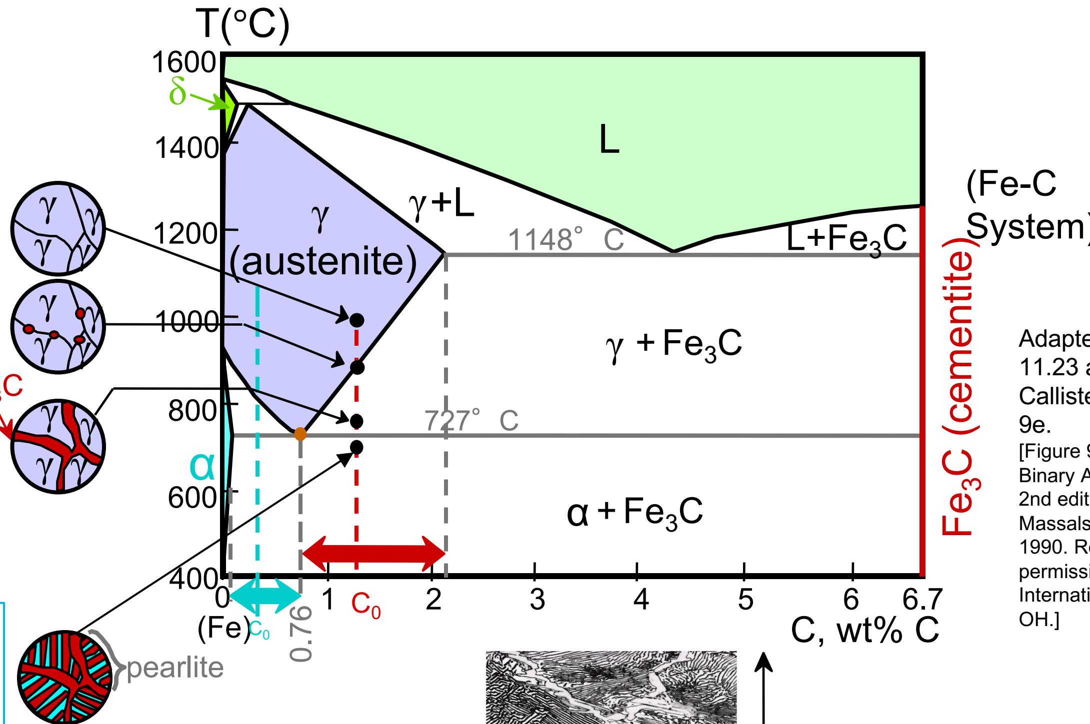
Hypereutectoid Steel (Microstructure)

Again, we start with a fully austenitic polycrystal

Fe_3C particles form along γ boundaries

Fe_3C grows in size

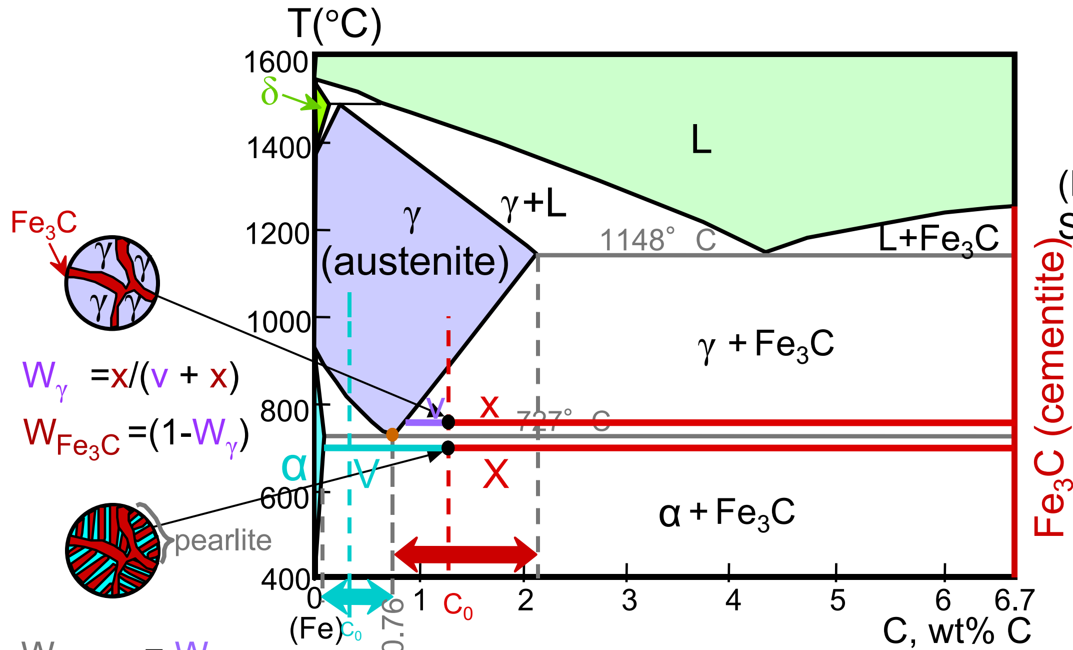
Remaining gamma transforms in to pearlite (Fe_3C+ γ layers)



Adapted from Figs. 11.23 and 11.31, Callister & Rethwisch 9e.
[Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]

Adapted from Fig. 11.32, Callister & Rethwisch 9e. (Copyright 1971 by United States Steel Corporation.)

Hypereutectoid Steel (Rule III)



$W_\gamma = x/(v + x)$

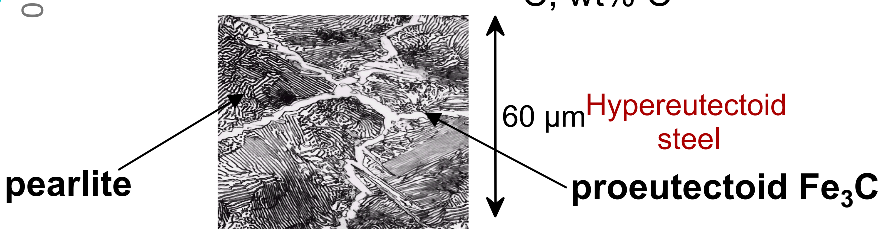
$W_{Fe_3C} = (1 - W_\gamma)$

$W_{pearlite} = W_\gamma$

$W_\alpha = X/(V + X)$

$W_{Fe_3C'} = (1 - W_\alpha)$

Adapted from Figs. 11.23 and 11.31, Callister & Rethwisch 9e.
[Figure 9.24 adapted from Binary Alloy Phase Diagrams, 2nd edition, Vol. 1, T. B. Massalski (Editor-in-Chief), 1990. Reprinted by permission of ASM International, Materials Park, OH.]



Adapted from Fig. 11.32, Callister & Rethwisch 9e. (Copyright 1971 by United States Steel Corporation.)

Summary

- Phase diagram provides three four different types of information
  - What phase(s) is (are) present given the conditions (temp, pressure, composition)
  - Invariant point
  - Lever rule
  - Metastable phases
  - Gibbs phase rule
- Unary and binary systems; isomorphous system; eutectic systems
- As temperature drops at a fixed pressure, microstructure develops
  - Polycrystalline of single phase
  - Eutectic structure; eutectoid structure
- Application to Fe-C system.
  - Alpha-ferrite, gamma-austenite, Fe3C-cementite
  - Pearlite; primary phase (proeutectoid)
  - Iron, cast iron, steel.