2019 Fall

Introduction to Materials Science and Engineering

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SUMMARY Chapter 10: Failure

- Engineering materials not as strong as predicted by theory
- **Flaws** act as stress concentrators that cause failure at stresses lower than theoretical values.
- **Sharp corners** produce large stress concentrations and premature failure.
- **Failure type depends on T and σ :**

  -**For simple fracture** (noncyclic σ and $T < 0.4T_m$), failure stress decreases with:
  - increased maximum flaw size,
  - decreased T,
  - increased rate of loading.

  - **For fatigue** (cyclic σ):
  - cycles to fail decreases as $\Delta\sigma$ increases.

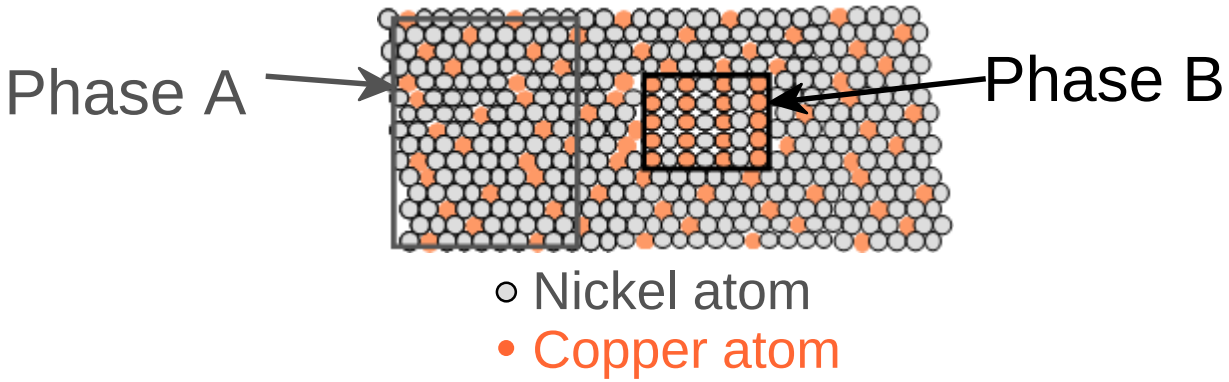
  - **For creep** ($T > 0.4T_m$):
  - time to rupture decreases as σ or T increases.

Chapter 11: Phase Diagrams

ISSUES TO ADDRESS...

- When we combine two elements...
  what is the resulting equilibrium state?
- In particular, if we specify...
  -- the composition (e.g., wt% Cu - wt% Ni), and
  -- the temperature (T)

  then...
  How many phases form?
  What is the composition of each phase?
  What is the amount of each phase?



What we will learn about

I. Component, Phase, Equilibrium

→ Phase diagram (Gibb's phase rule)

II. one component phase diagram

two component phase diagram

: solubility limit (Hume-Rothery Rule)

III. Isomorphous Binary Phase Diagram

: tie line, lever rule

IV. Binary-Eutectic Systems

V. Binary invariant reaction

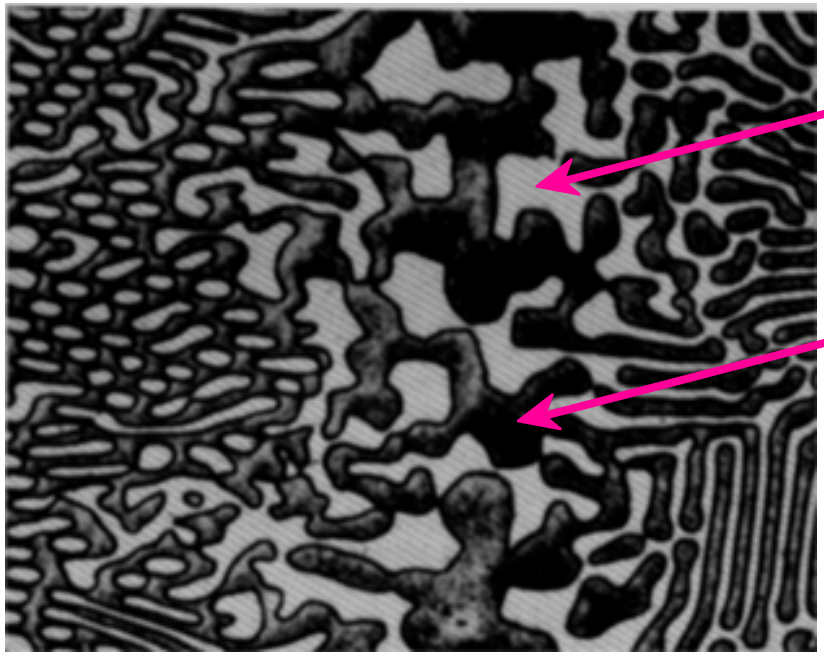
: Eutectic, Eutectoid, & Peritectic

- **Ternary, Quarternary phase diagram**
- **Phase transformation**

I-a. Components and Phases

- Components:
  The **elements** or **compounds** which are present in the alloy (e.g., Al and Cu)
- Phases:
  The **physically** and **chemically distinct material regions** that form (e.g., *α* and *β*).

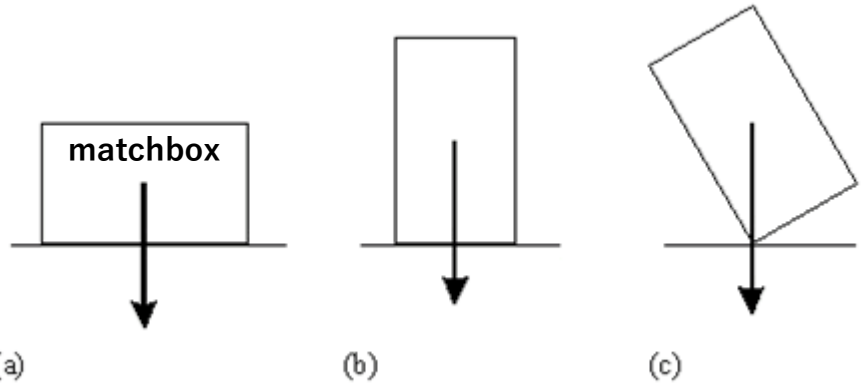
Aluminum-Copper Alloy



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

b. Equilibrium

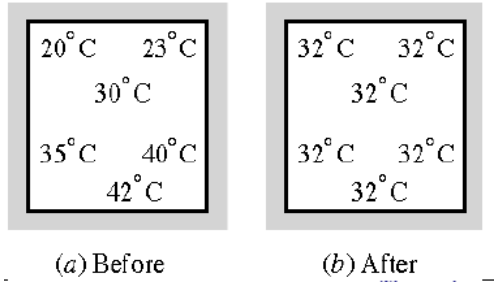
Mechanical equilibrium



: total potential energy of the system is a minimum.

Thermal equilibrium

: absence of temperature gradients in the system



Chemical equilibrium

: no further reaction occurs between the reacting substances
i.e. the forward and reverse rates of reaction are equal.

Thermodynamic equilibrium

: the system is under mechanical, thermal and chemical equilibrium

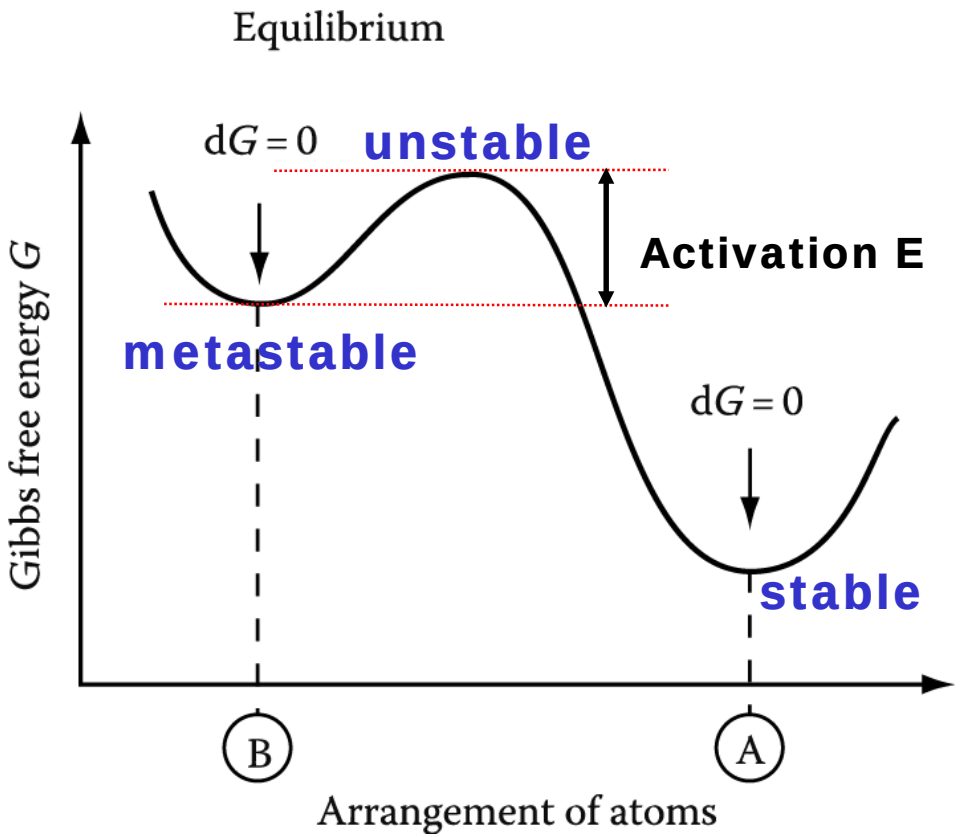
The properties of the system-P, T, V, concentrations-do not change with time.

Equilibrium

$dG = 0$

Lowest possible value of Gibb's Free Energy

No desire to change ad infinitum



Phase Transformation

$\Delta G = G_2 - G_1 < 0$

c. Phase diagram & Gibbs phase rule

- ***phase diagram***: *graphical representation of the phases present and the ranges in composition, temperature, and pressure over which the phases are stable*
- ***Gibbs phase rule: F=C-P+2***

  C: # components, P: # phases in equilibrium

  F: degree of freedom (temp., press., composition)

ex) H_2O, *C=1, F=C-P+2=3-P*

1 phase F=2

2 phase F=1

3 phase F=0 (invariant)

** pressure or temperature constant →* ***F=C-P+1***

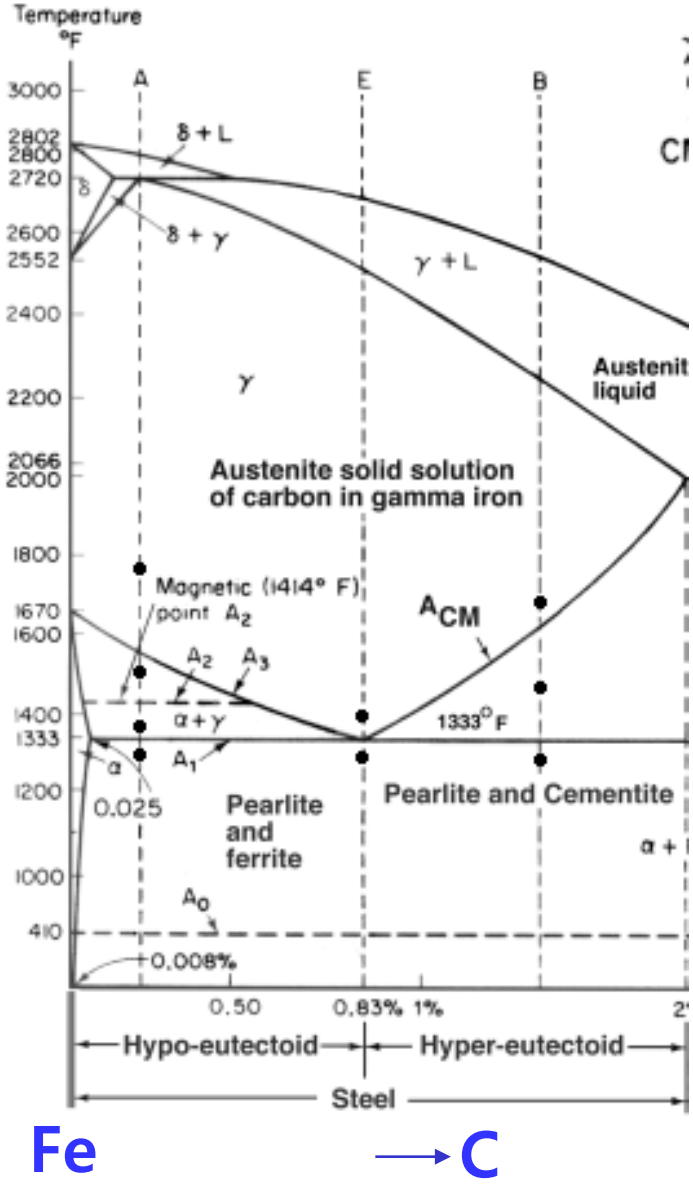
II-a. Single component system

One element (Al, Fe)

One type of molecule (H_2O)

- Allotropic forms?

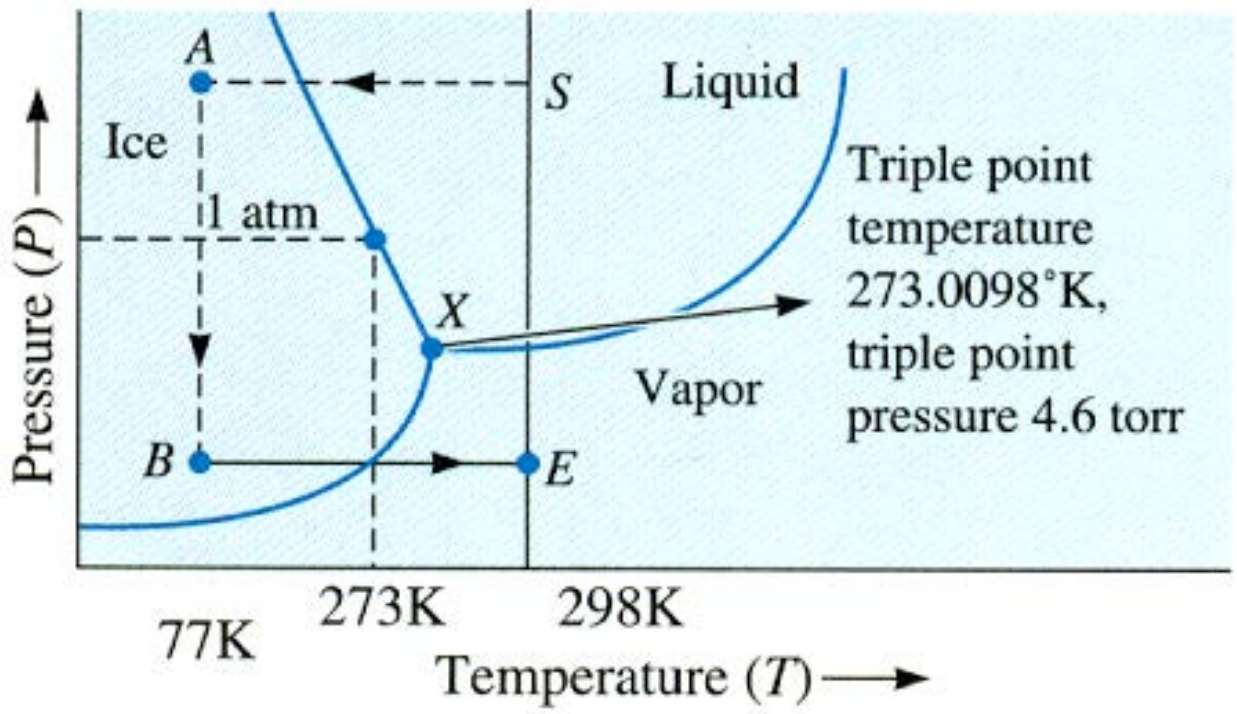
- How is phase stability measured?



$$G = H - TS$$

➡ Gibbs Free Energy as a Function of Temp.

One Component Phase Diagram



Pressure-temperature diagram for H_2O. Notice the solid-liquid line sloping to the left. At normal pressure (1 atm or 760 torr), the melting temperature is 273 K. A possible scheme for freeze drying is shown as starting with point S and following the dashed line to the left.

Equilibrium and non-equilibrium states by heating

Multi-component system:

b: What are binary systems?

"Mixture vs. Solution vs. Compound"

*** Single component system** One element (Al, Fe), One type of molecule (H_2O)

: Equilibrium depends on pressure and temperature.

*** Binary system (two components)** → A, B

: Equilibrium depends on not only pressure and temperature but also composition.

- **Mixture** ; A – A, B – B ; → the physical combination of two or more substances on which the identities and boundaries are retained.

A B

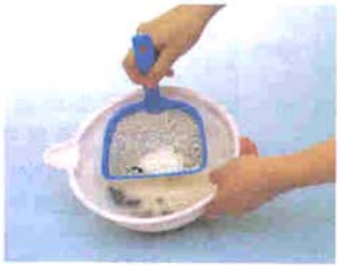
Alluvial mining

사금 채취

키질

Winnowing

wash rice



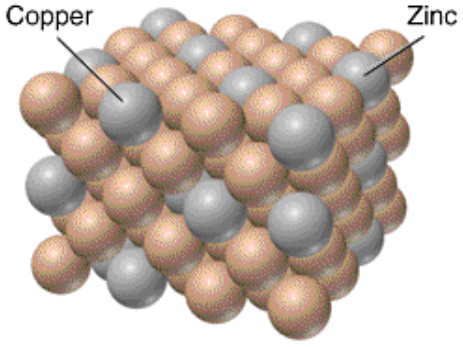
쌀 씻기

달걀 고르기

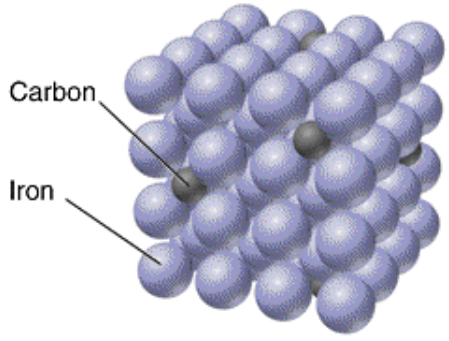
Select egg

- **Solution ; A – A – A ; → atomic scale mixture/ Random distribution**

  A – B – A Solid solution : substitutional or interstitial



A Brass, a substitutional alloy

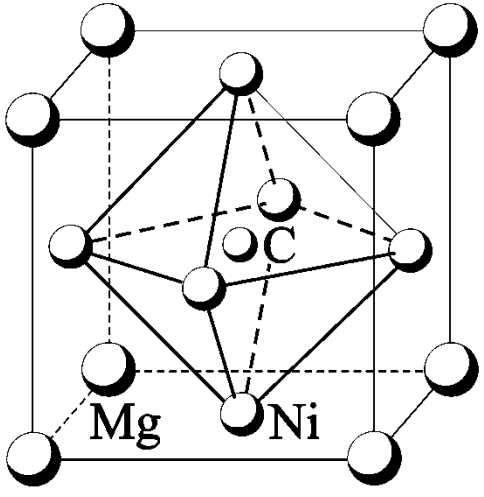


B Carbon steel, an interstitial alloy

- **Compound ; A – B – A – B ; → fixed A, B positions/ Ordered state**

B – A – B – A

MgCNi3



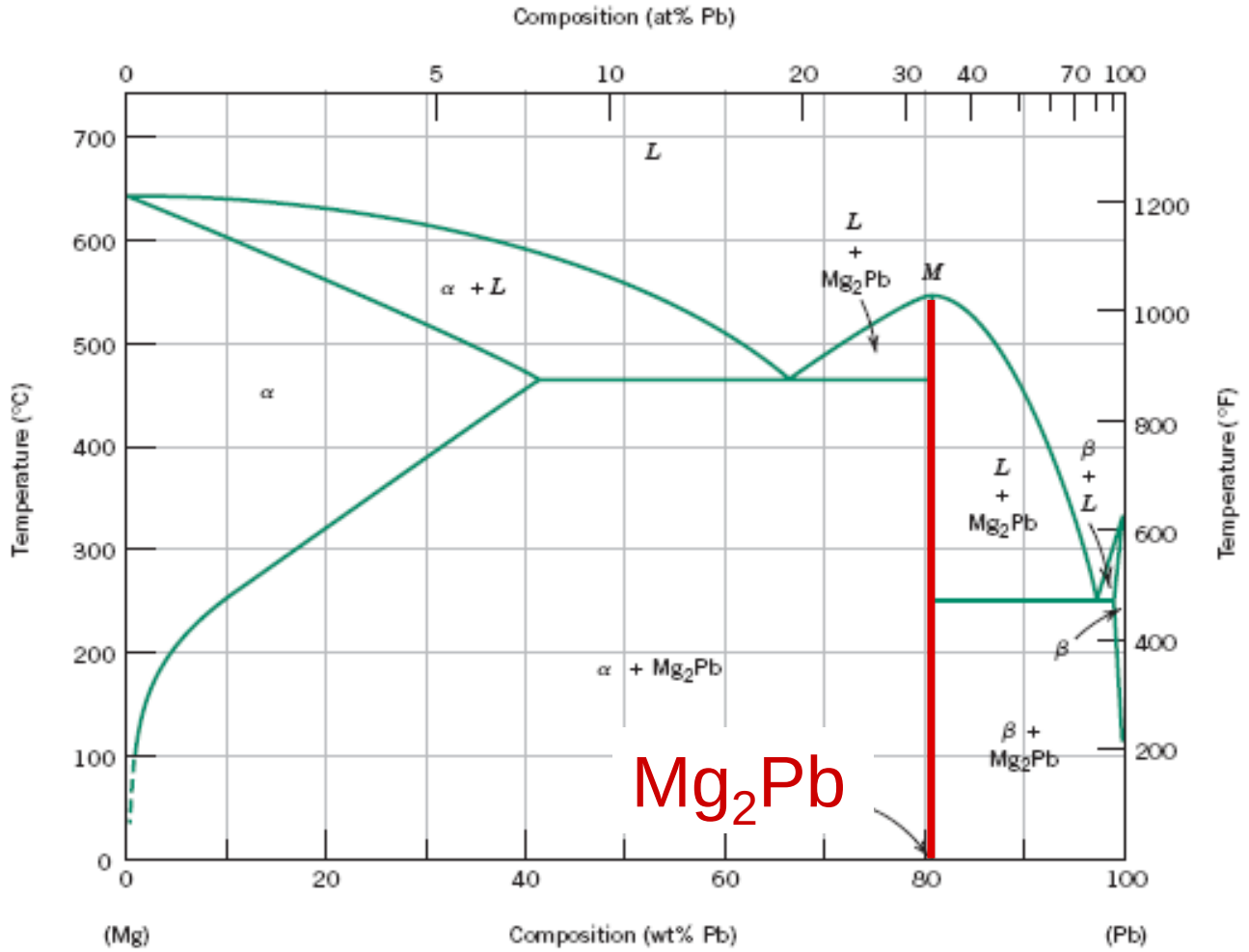
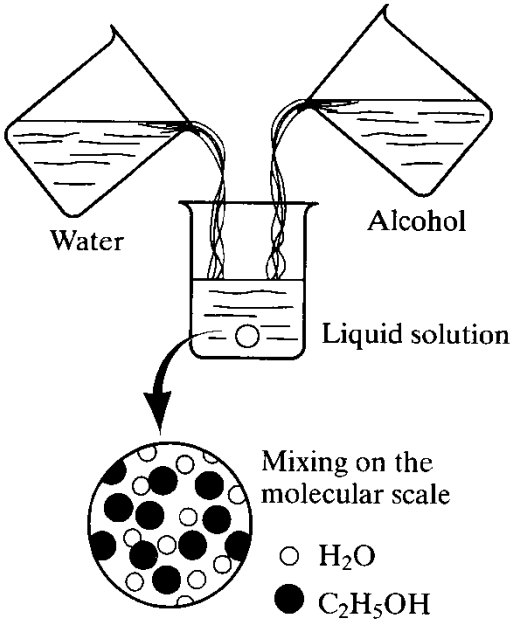


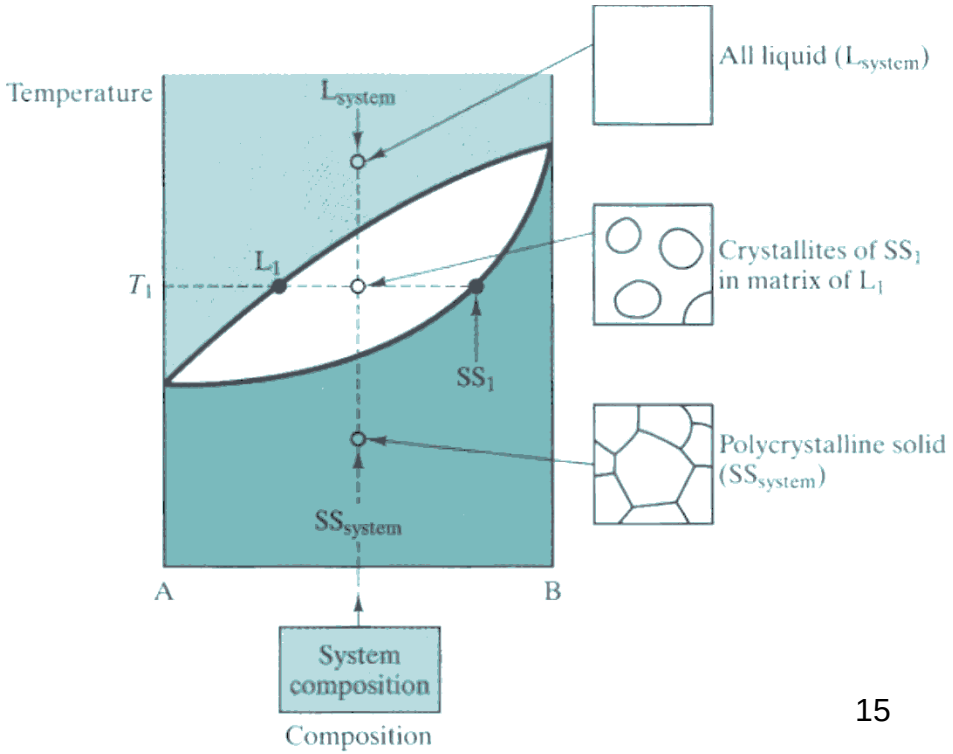
Fig. 11.19, *Callister & Rethwisch 9e.* [Adapted from *Phase Diagrams of Binary Magnesium Alloys*, A. A. Nayeb-Hashemi and J. B. Clark (Editors), 1988. Reprinted by permission of ASM International, Materials Park, OH.]

Note: intermetallic compound exists as a line on the diagram - not an area - because of stoichiometry (i.e. composition of a compound is a fixed value).

c. Solubility

- Unlimited Solubility
  - Hume Rothery' Conditions
    - Similar Size
    - Same Crystal Structure
    - Same Valance
    - Similar Electronegativity
  - Implies single phase
- Limited Solubility
  - Implies multiple phases
- No Solubility
  - oil and water region





Solubility Limit

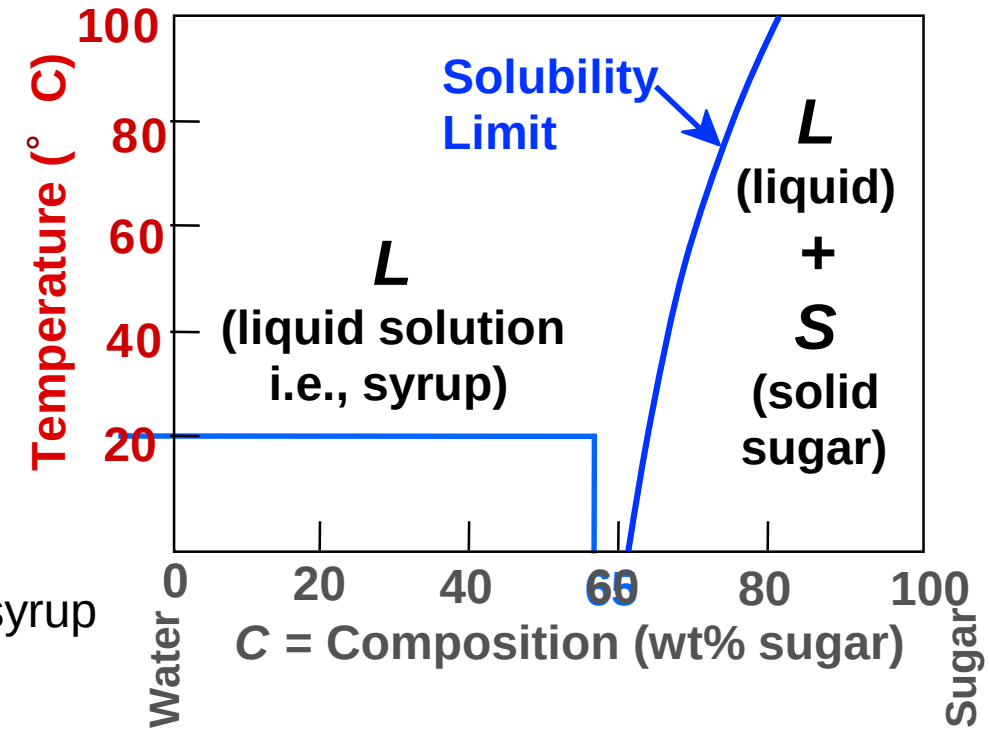
- Solubility Limit:
  Maximum concentration for which only a single phase solution exists.

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

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

Adapted from Fig. 11.1, *Callister & Rethwisch 9e.*

Sugar/Water Phase Diagram



Effect of Temperature & Composition

- Altering *T* can change # of phases: path *A* to *B*.
- Altering *C* can change # of phases: path *B* to *D*.

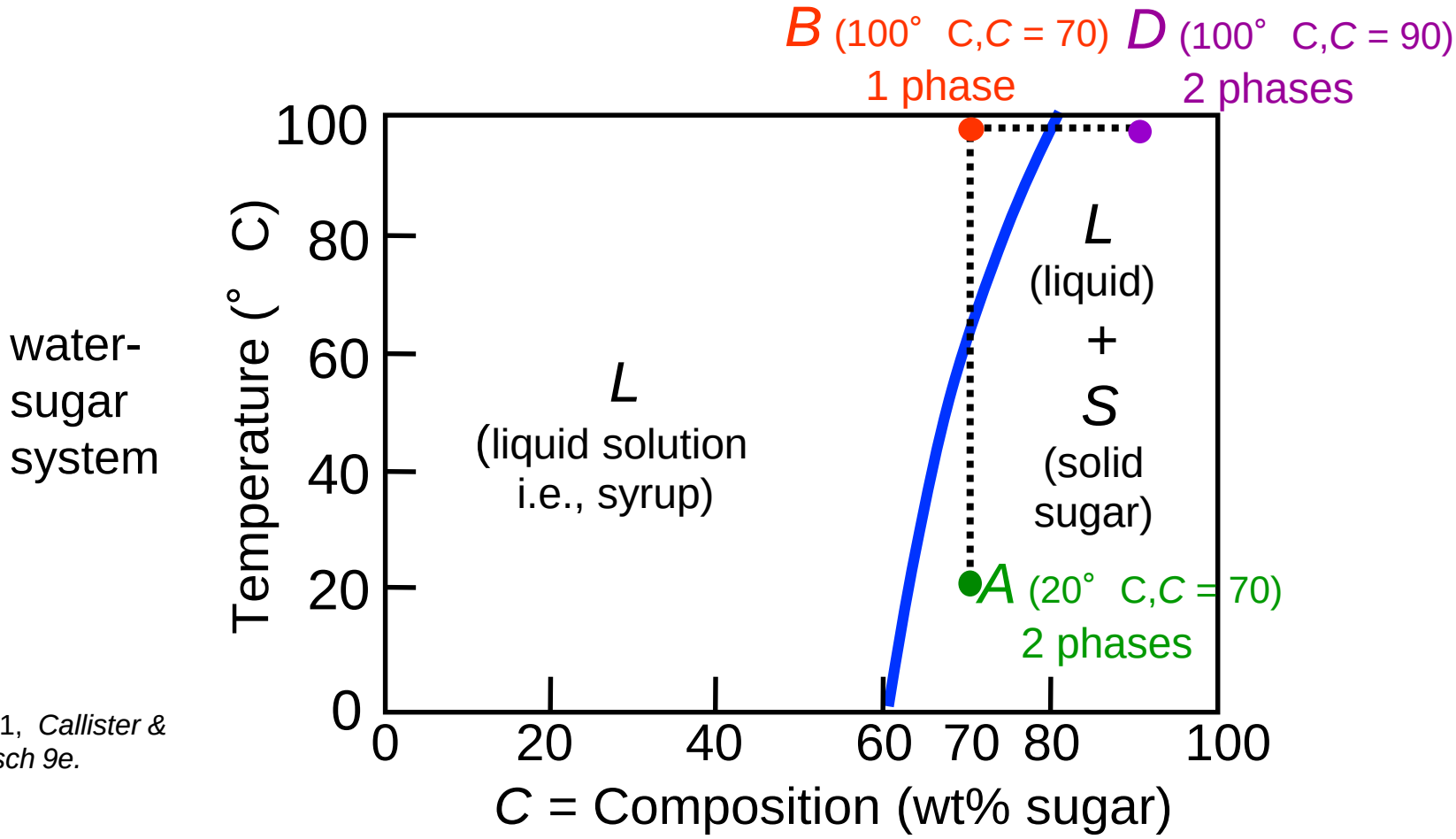
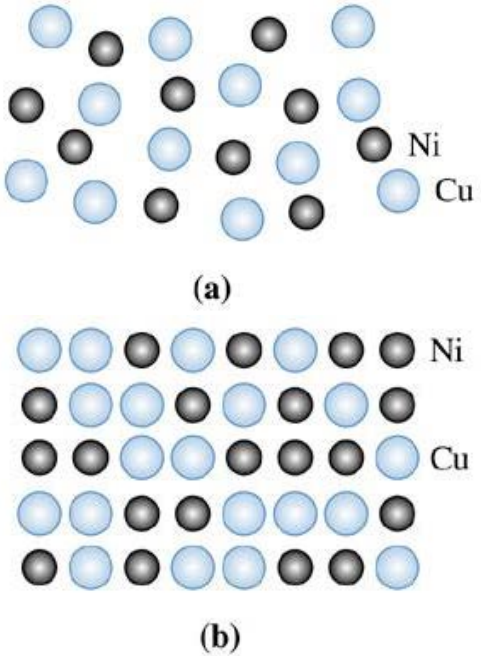


Fig. 11.1, *Callister & Rethwisch 9e.*

Solubility Limit



(a) Liquid copper and liquid nickel are completely soluble in each other.

(b) Solid copper-nickel alloys display complete solid solubility, with copper and nickel atoms occupying random lattice sites.

(c) In copper-zinc alloys containing more than 30% Zn, a second phase forms because of the limited solubility of zinc in copper.

d. Criteria for Solid Solubility: Hume-Rothery Rule

Empirical rules for substitutional solid-solution formation were identified from experiment that are not exact, but give an expectation of formation.
Briefly,

1) Atomic Size Factor **The 15% Rule**

If "size difference" of elements are greater than ±15%, the lattice distortions (i.e. local lattice strain) are too big and solid-solution will not be favored.

$$\text{DR\%} = \frac{r_{solute} - r_{solvent}}{r_{solvent}} \times 100\% \quad < \quad \pm 15\%$$ **will not disallow formation.**

2) Crystal Structure **Like elemental crystal structures are better**

For appreciable solubility, the crystal structure for metals must be the same.

3) Electronegativity **DE ~ 0 favors solid-solution.**

The more electropositive one element and the more electronegative the other, then "intermetallic compounds" (order alloys) are more likely.

4) Valences **Higher in lower alright. Lower in higher, it's a fight.**

A metal will dissolve another metal of higher valency more than one of lower valency.

Phase Equilibria

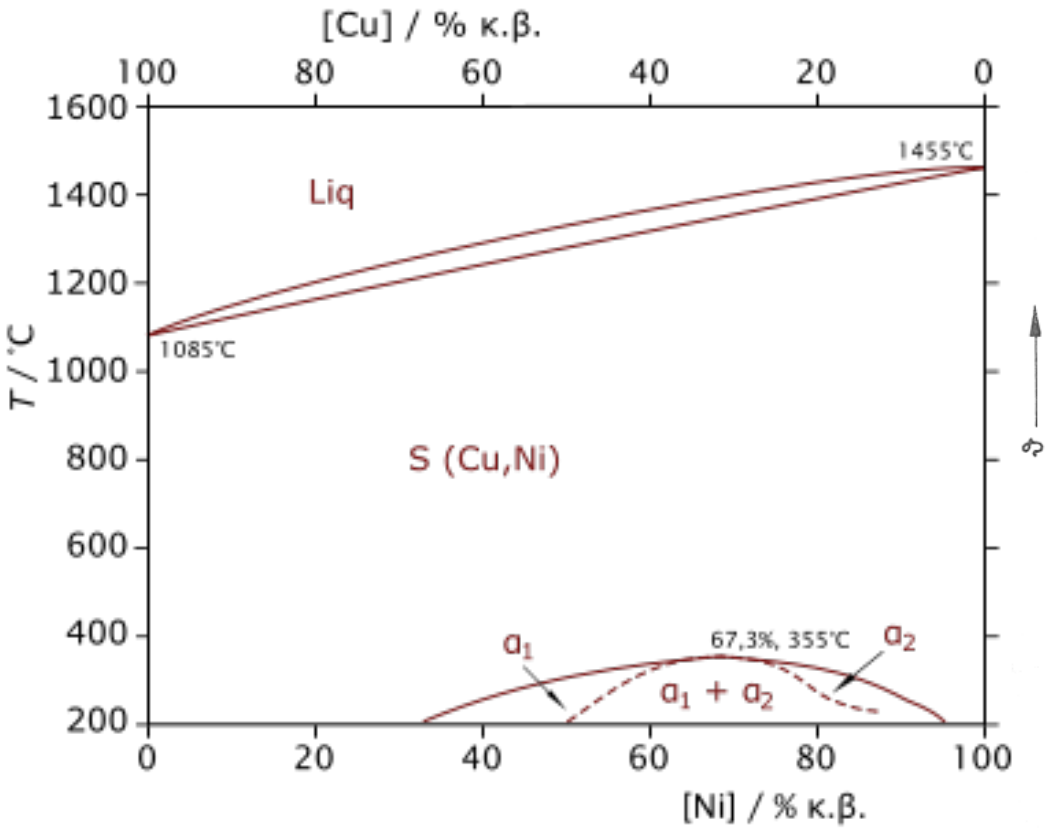
Complete mixture

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

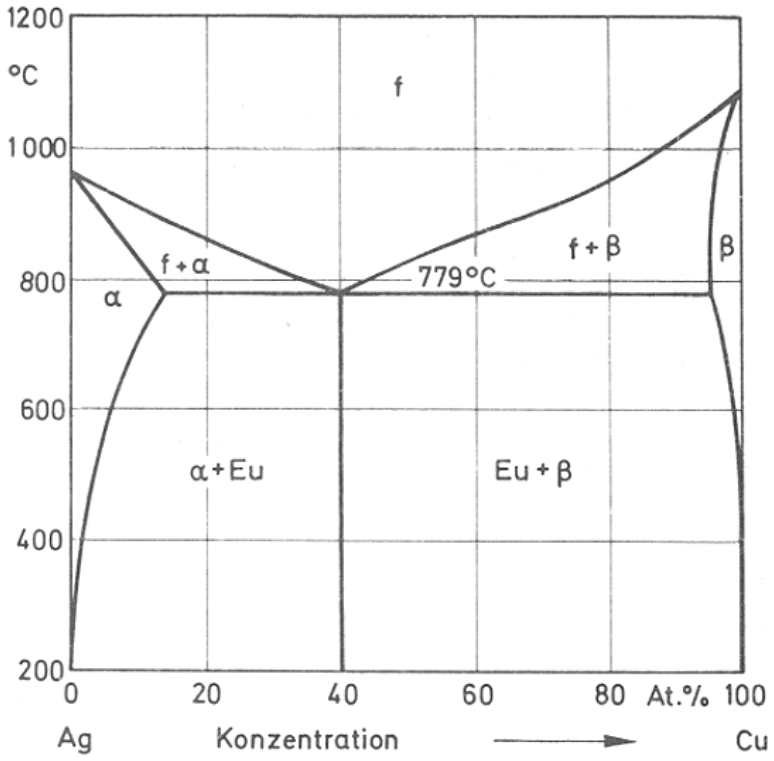
	Crystal Structure	Electro-negativity	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally miscible in all proportions.

Cu-Ni Alloys



Cu-Ag Alloys



complete solid solution

limited solid solution

e. Complete immiscibility of two metals does not exist.

: The solubility of one metal in another may be so low (e.g. Cu in Ge $<10^{-7}$ at%.)
that it is difficult to detect experimentally, but there will always be a measure of solubility.

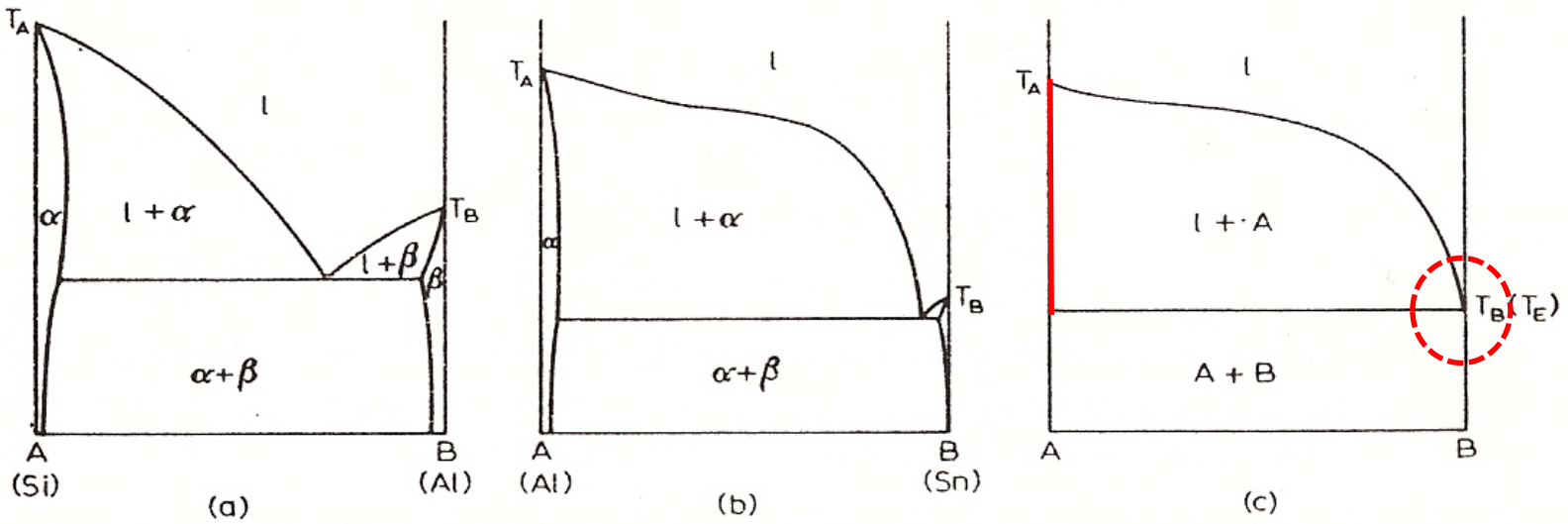


Fig. 53. Evolution of the limiting form of a binary eutectic phase diagram.

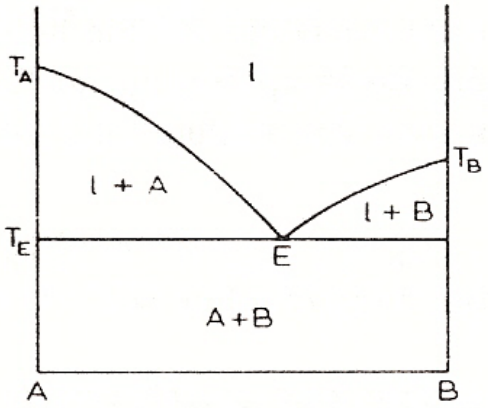
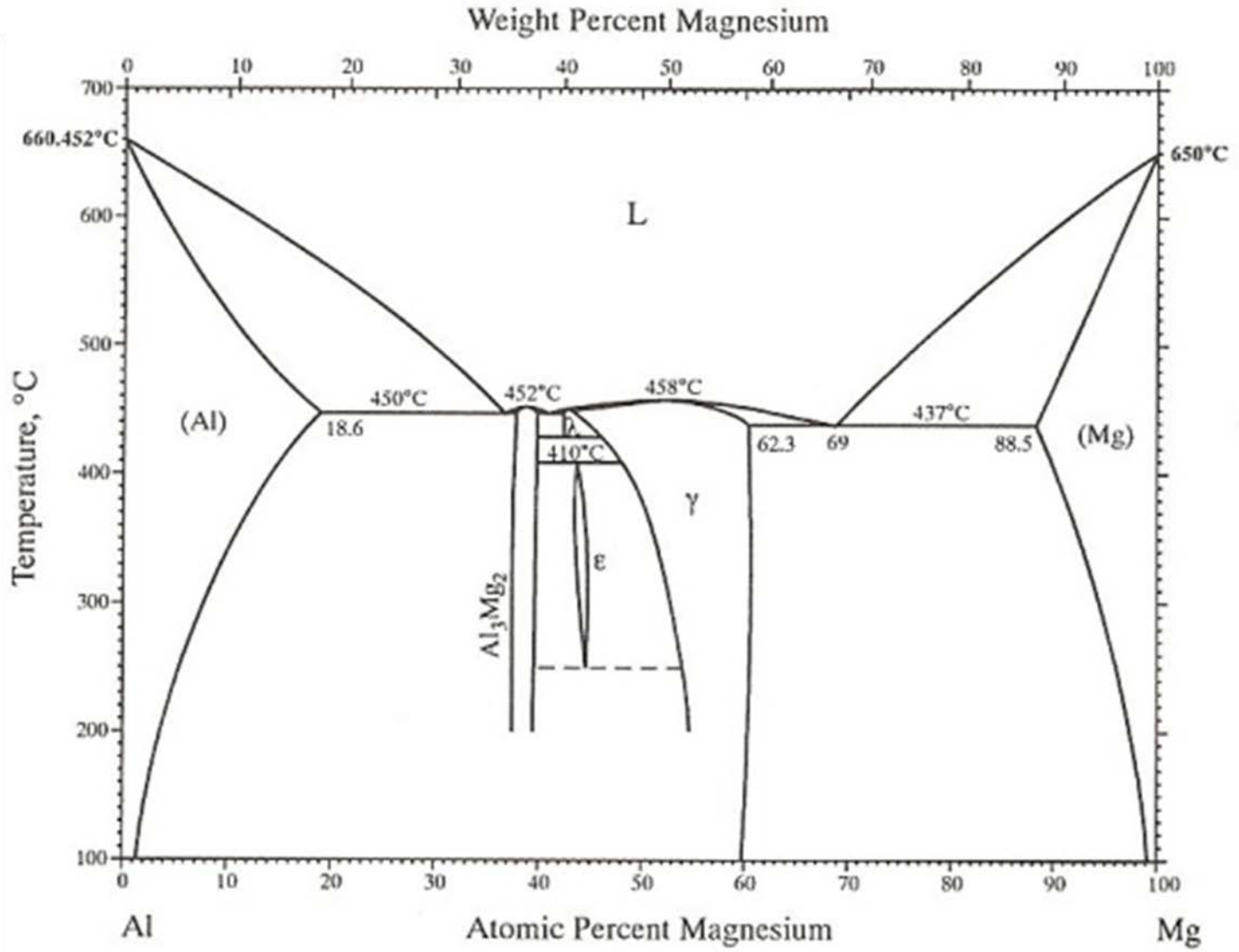
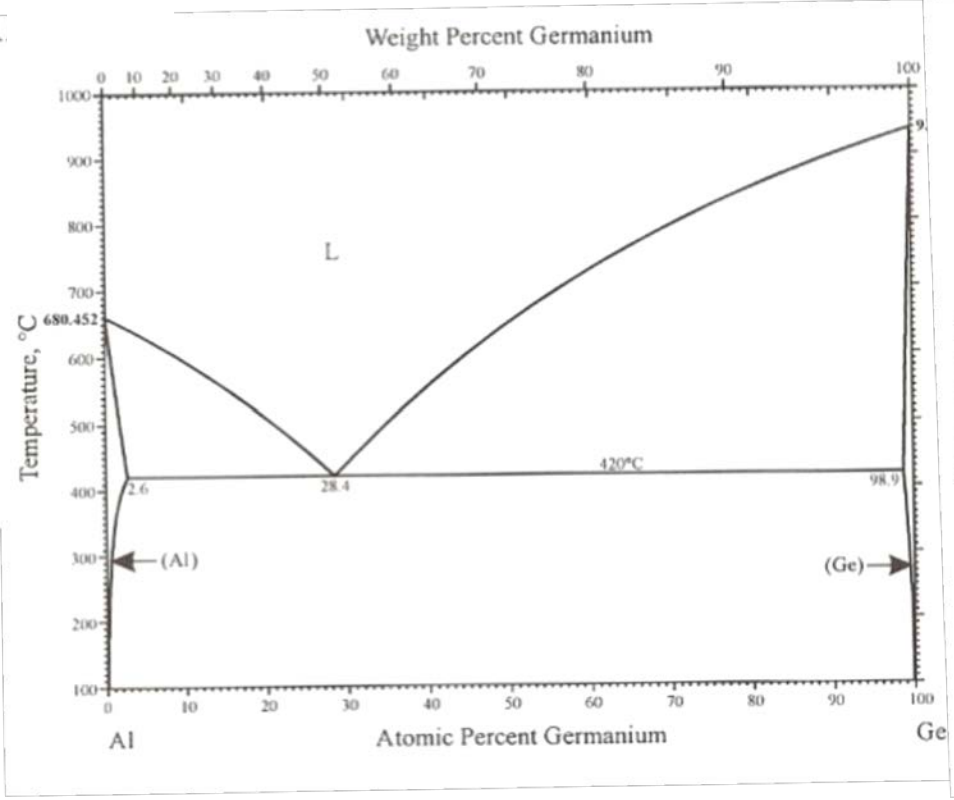
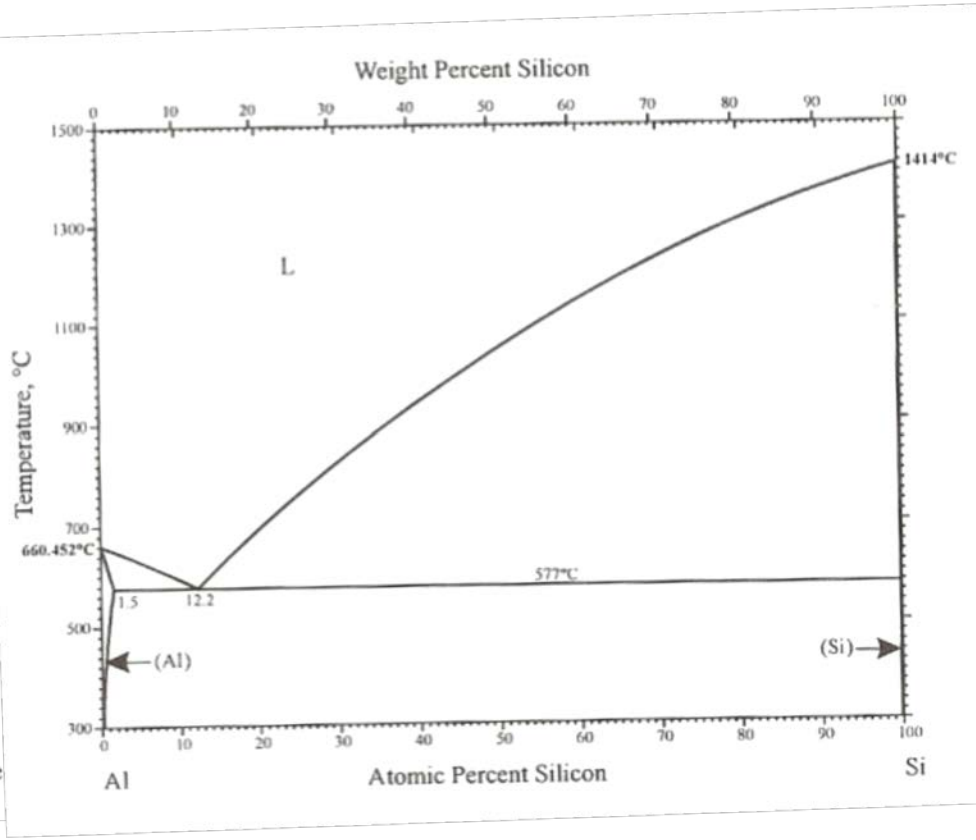
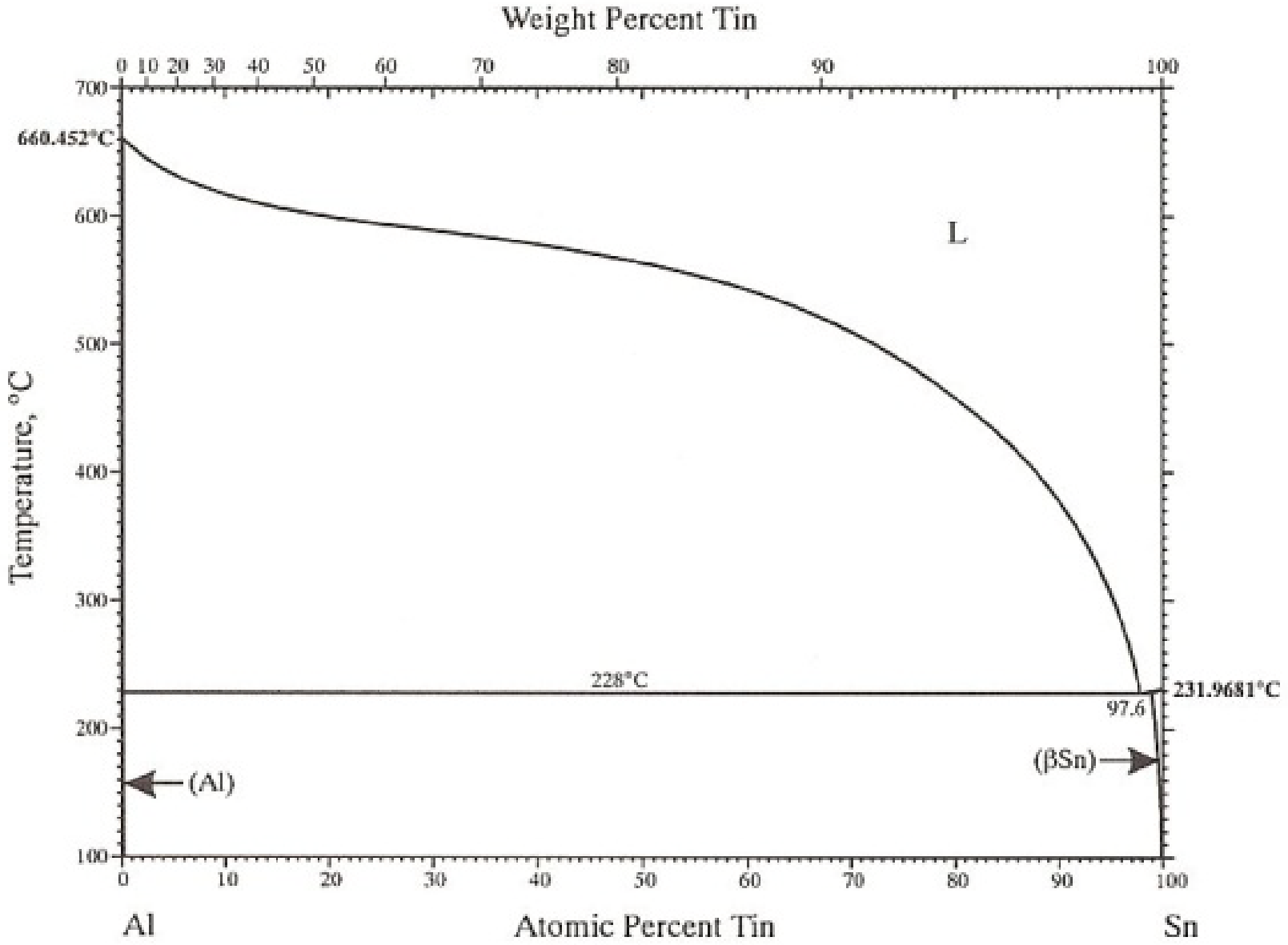


Fig. 54. Impossible form of a binary eutectic phase diagram.


Weight Percent Magnesium
0
10
20
30
40
50
60
70
80
90
100
700
660.452°C
650°C
600
500
400
300
200
100
L
(Al)
450°C
18.6
452°C
458°C
437°C
62.3
69
88.5
(Mg)
410°C
γ
ε
Al_3Mg_2
Temperature, °C
Al
Atomic Percent Magnesium
Mg


Weight Percent Germanium
Temperature, °C
L
680.452
420°C
2.6
28.4
98.9
(Al)
(Ge)
Al
Atomic Percent Germanium
Ge

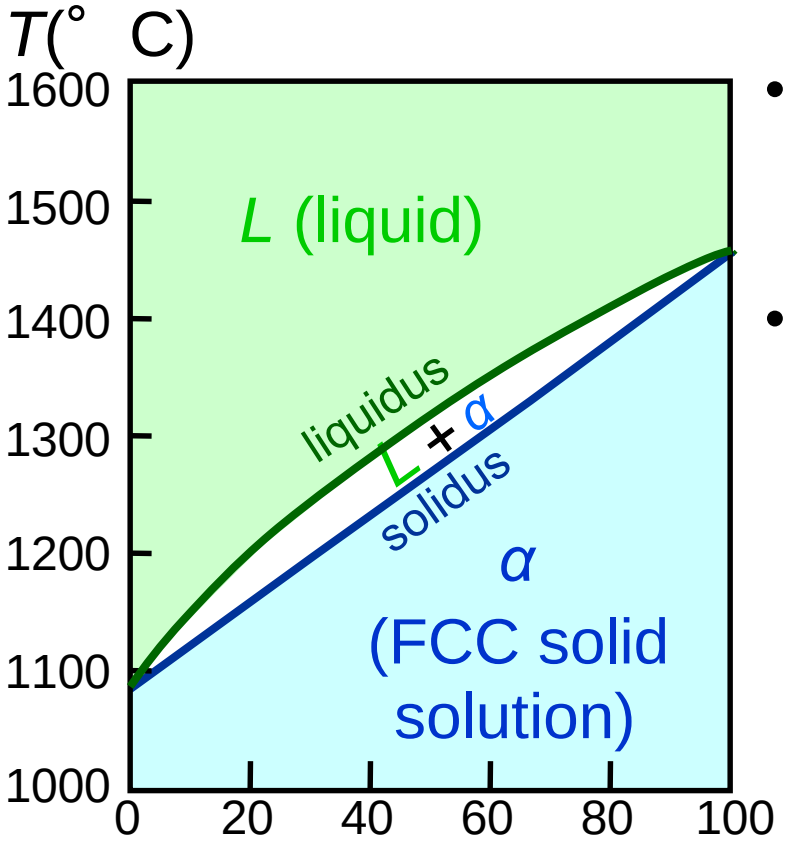

Weight Percent Silicon
Temperature, °C
L
1414°C
660.452°C
577°C
1.5
12.2
(Al)
(Si)
Al
Atomic Percent Silicon
Si


Weight Percent Tin
0 10 20 30 40 50 60 70 80 90 100
700
660.452°C
600
500
400
300
200
100
Temperature, °C
L
228°C
231.9681°C
97.6
(βSn)
(Al)
0 10 20 30 40 50 60 70 80 90 100
Al
Atomic Percent Tin
Sn

III. Isomorphous Binary Phase Diagram

- Indicate phases as a function of *T*, *C*, and *P*.
- For this course:
  - binary systems: just 2 components (Cu and Ni).
  - independent variables: *T* and *C* (*P* = 1 atm is almost always used).

Phase Diagram for Cu-Ni system



- 2 phases:
  - *L* (liquid)
  - *α* (FCC solid solution)
- 3 different phase fields:
  - *L*
  - *L* + *α*
  - *α*

Fig. 11.3(a), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

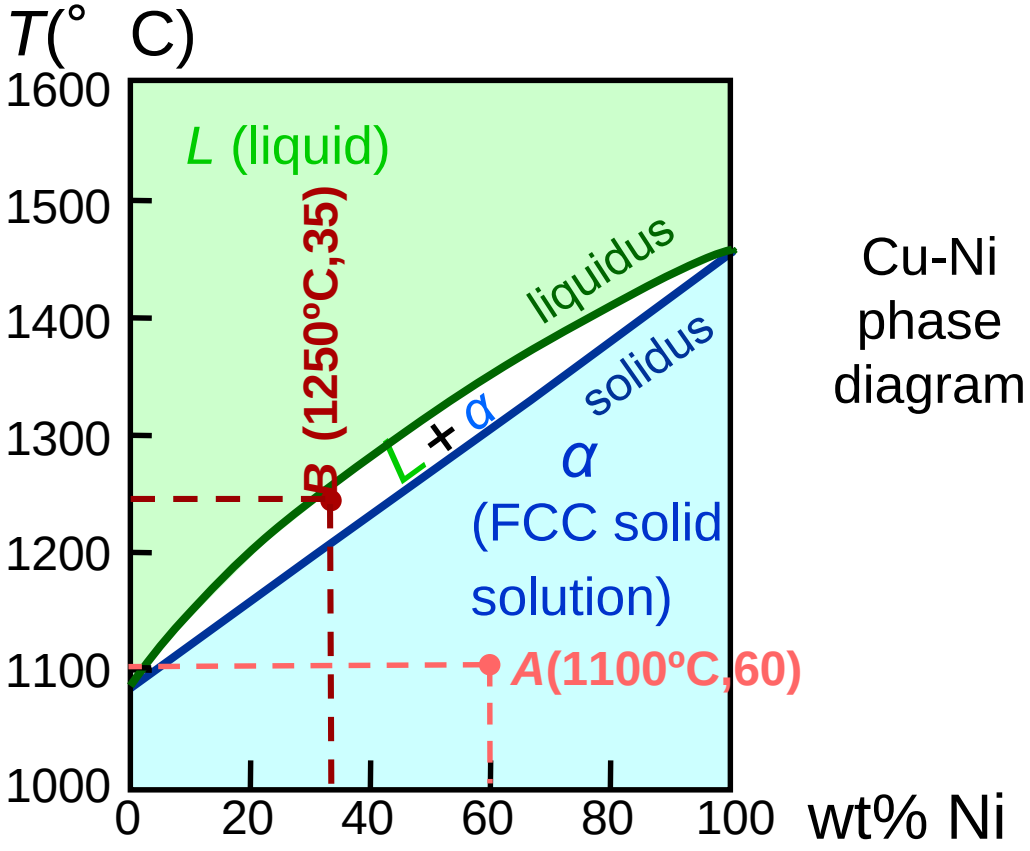
a. Determination of phase(s) present

- Rule 1: If we know T and C_o, 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: $L + \alpha$



Cu-Ni phase diagram

Fig. 11.3(a), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

b. Determination of phase compositions

- Rule 2: If we know T and C_0, then we can determine:
  -- the composition of each phase.

- Examples:

  Consider C_0 = 35 wt% Ni

  At T_A = 1320°C:

  Only Liquid (L) present

  $C_L = C_0$ (= 35 wt% Ni)

  At T_D = 1190°C:

  Only Solid (α) present

  $C_\alpha = C_0$ (= 35 wt% Ni)

  At T_B = 1250°C:

  Both α and L present

  $C_L = C_{liquidus}$ (= 32 wt% Ni)

  $C_\alpha = C_{solidus}$ (= 43 wt% Ni)

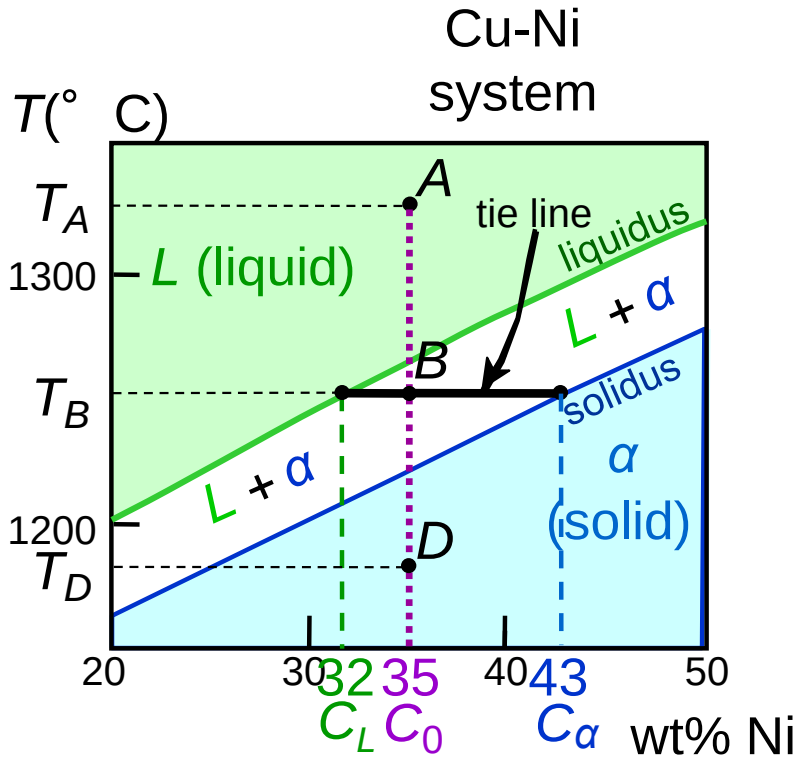


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

c. Determination of phase weight fractions

- Rule 3: If we know T and C_0, then can determine:
  -- the weight fraction of each phase.
- Examples:

Consider C_0 = 35 wt% Ni

At T_A : Only Liquid (L) present

$W_L = 1.00, W_\alpha = 0$

At T_D : Only Solid (α) present

$W_L = 0, W_\alpha = 1.00$

At T_B : Both α and L present

$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 0.73$$

$$W_\alpha = \frac{R}{R+S} = 0.27$$

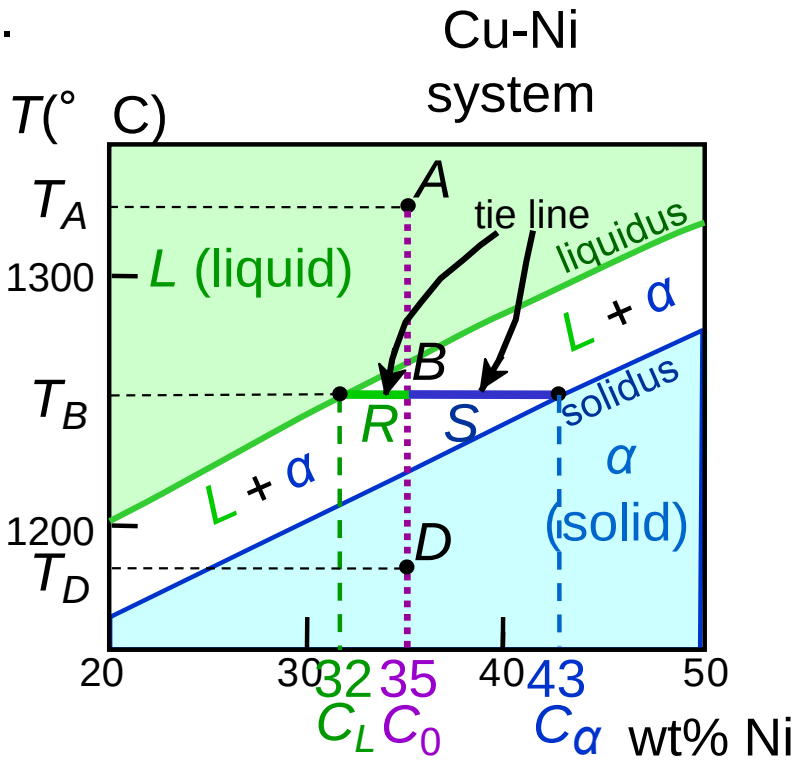
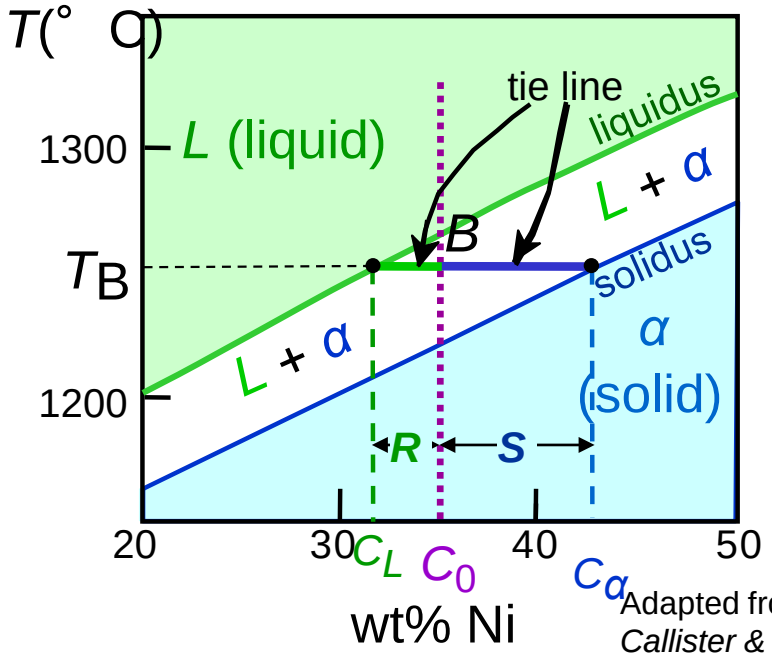


Fig. 11.3(b), *Callister & Rethwisch 9e.* (Adapted from *Phase Diagrams of Binary Nickel Alloys*, P. Nash, Editor, 1991. Reprinted by permission of ASM International, Materials Park, OH.)

The Lever Rule

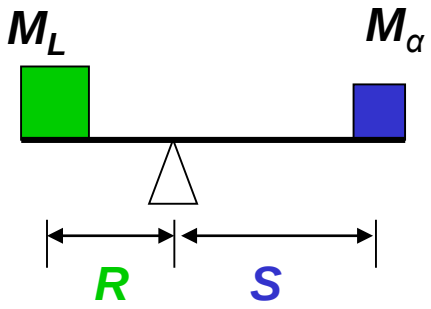
- Tie line – connects the phases in equilibrium with each other – also sometimes called an isotherm



Adapted from Fig. 11.3(b), *Callister & Rethwisch 9e.*

What fraction of each phase?

Think of the tie line as a lever (teeter-totter)



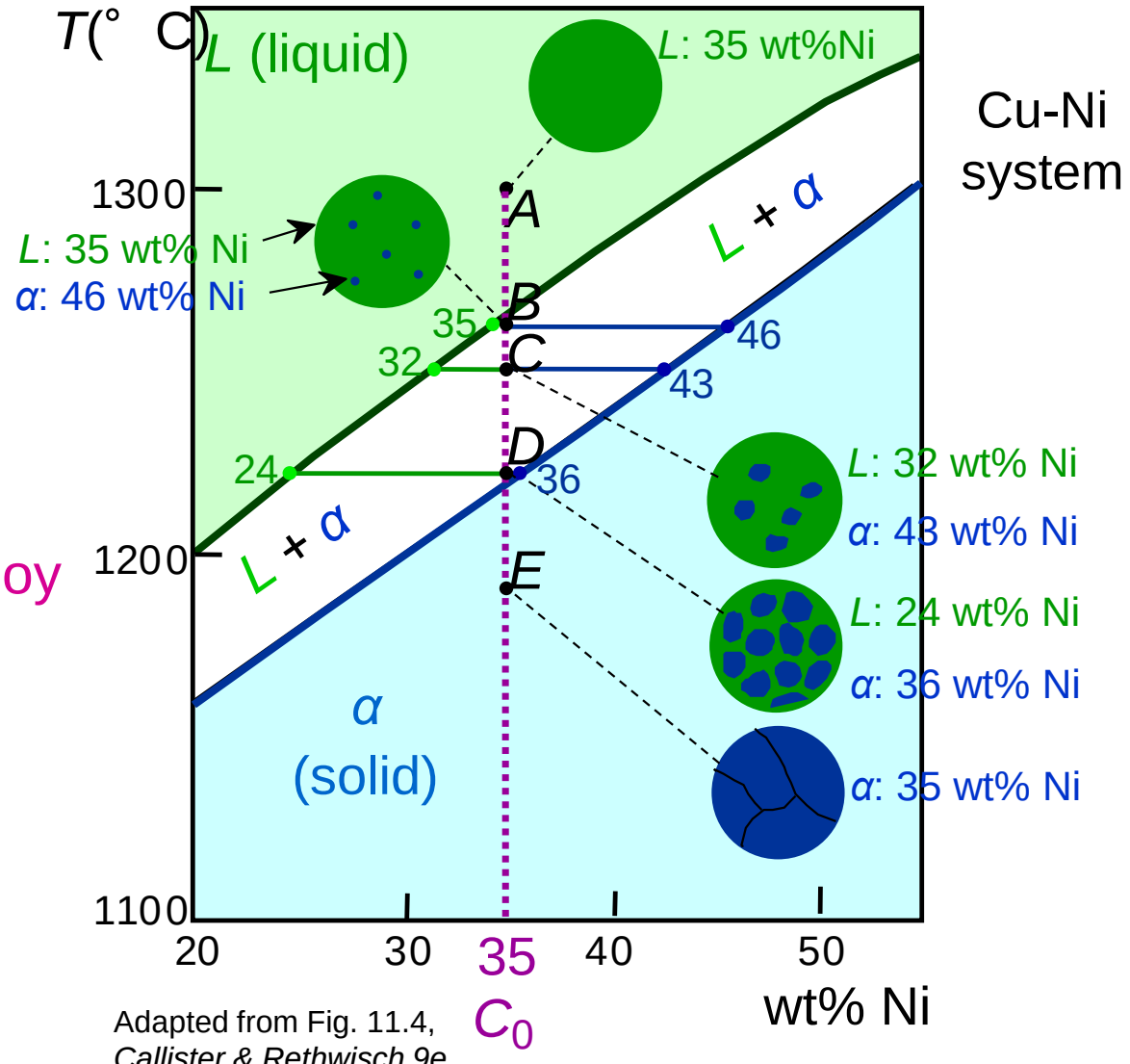
$$M_\alpha \times S = M_L \times R$$

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

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

d. Cooling of a Cu-Ni Alloy

- Phase diagram: Cu-Ni system.
- Consider microstuctural changes that accompany the cooling of a C_0 = 35 wt% Ni alloy



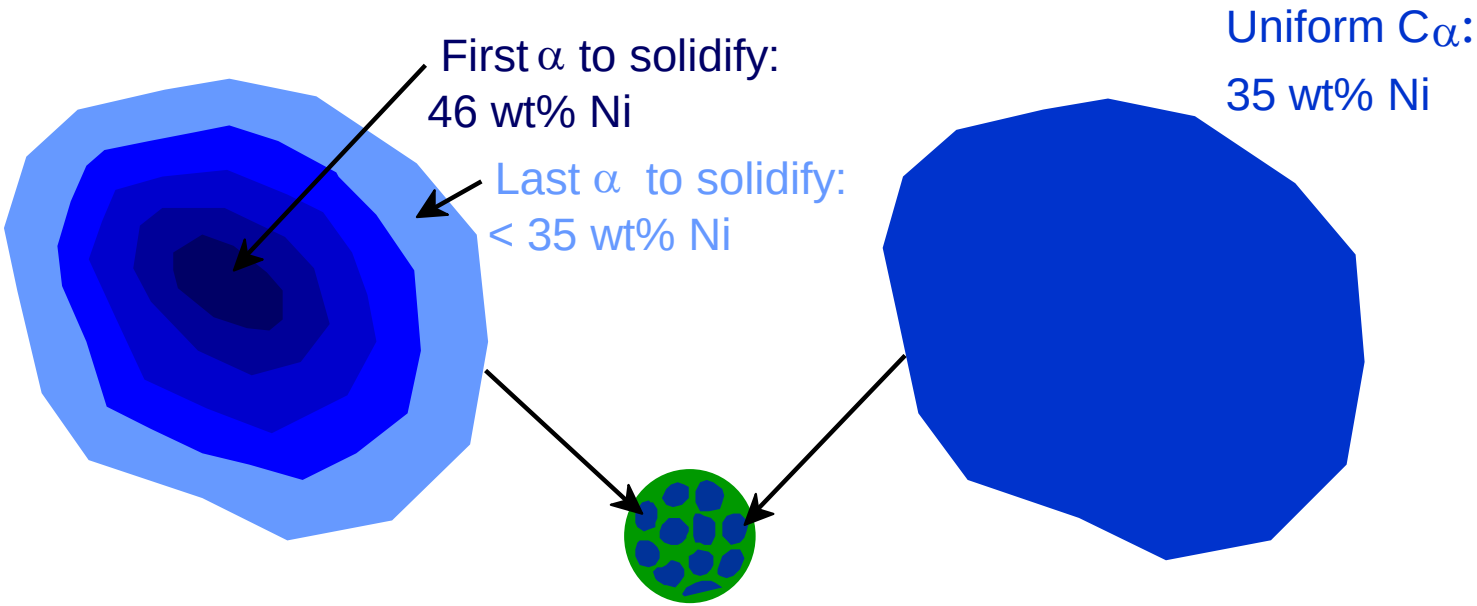
Adapted from Fig. 11.4, *Callister & Rethwisch 9e.*

e. Cored vs Equilibrium Phases

- C_α changes as we solidify.
- Cu-Ni case: First α to solidify has C_α = 46 wt% Ni.
  Last α to solidify has C_α = 35 wt% Ni.

- Fast rate of cooling:
  Cored structure

- Slow rate of cooling:
  Equilibrium structure



f. Relationship Between Properties and the Phase Diagram

- **Solid-solution strengthening - Increasing the strength of a metallic material via the formation of a solid solution.**

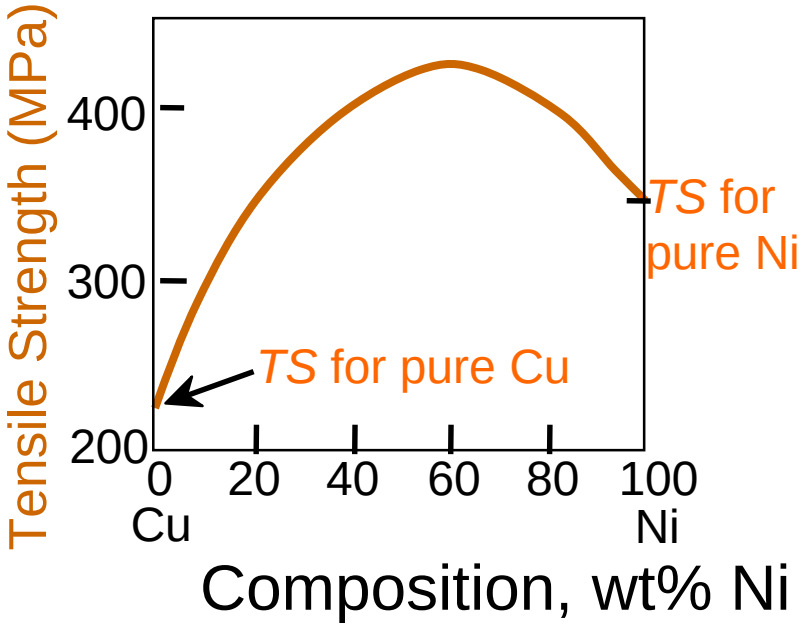
- **Dispersion strengthening - Strengthening, typically used in metallic materials, by the formation of ultra-fine dispersions of a second phase.**

Mechanical Properties: Cu-Ni System

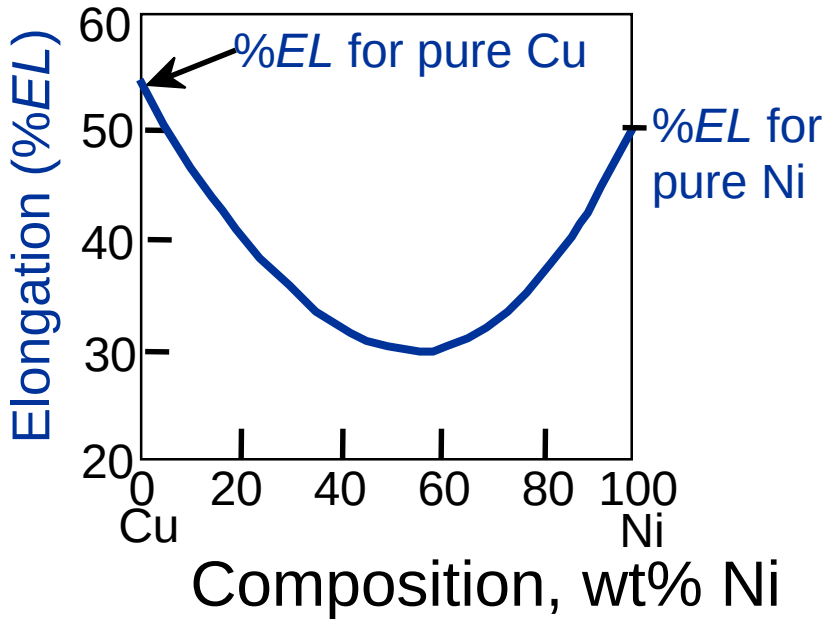
- Effect of solid solution strengthening on:

  -- Tensile strength (*TS*)

  -- Ductility (%*EL*)

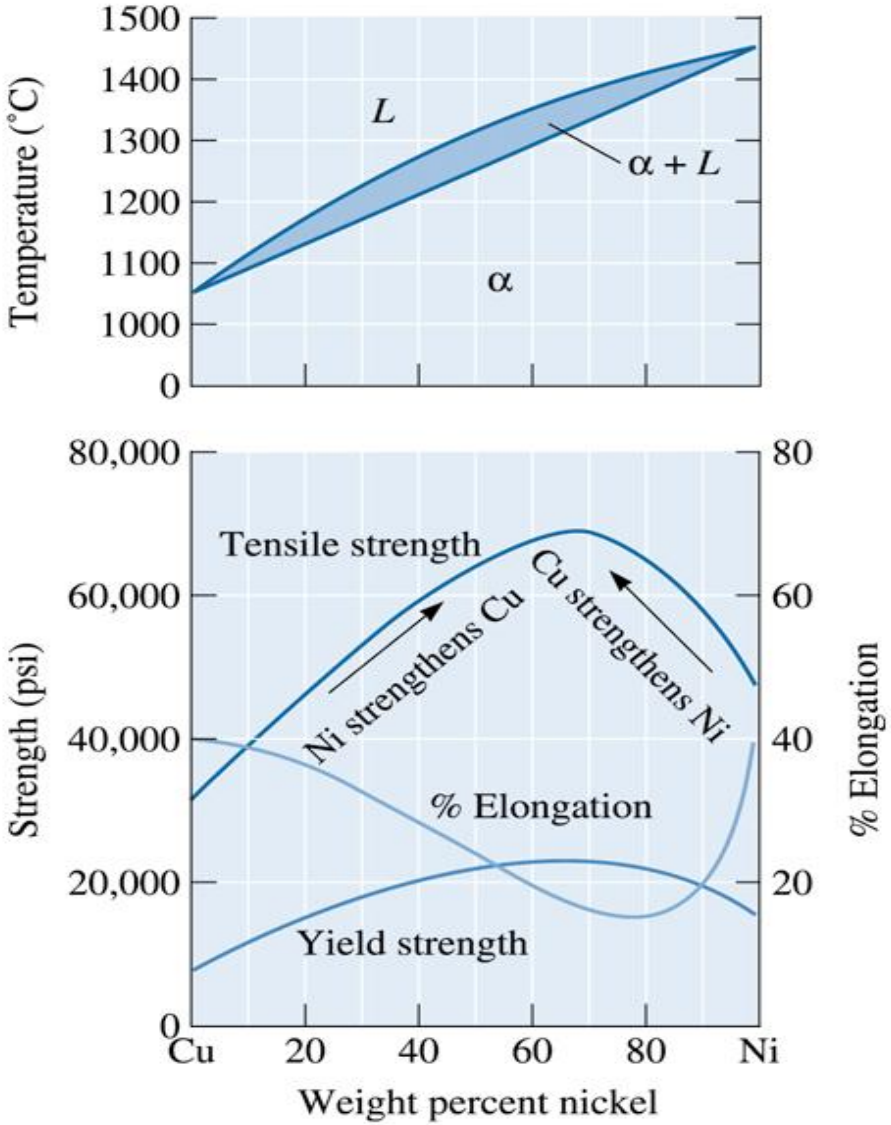


Adapted from Fig. 11.5(a), *Callister & Rethwisch 9e.*



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

Mechanical Properties: Cu-Ni System



Copper is strengthened by up to 60% Ni and nickel is strengthened by up to 40% Cu.

Summary

- Phase diagrams are useful tools to determine:
  -- the number and types of phases present,
  -- the composition of each phase,
  -- and the weight fraction of each phase
  given the temperature and composition of the system.

- The microstructure of an alloy depends on
  -- its composition, and
  -- whether or not cooling rate allows for maintenance of equilibrium.

- Important phase diagram phase transformations include eutectic, eutectoid, and peritectic.