PY2N20
Material Properties and Phase Diagrams
Lecture 5

P. Stamenov, PhD

School of Physics, TCD

Phase Diagrams - Introduction

- How much can be done with pure elemental compounds?

- How many combinations of elements could be imagined? – 2^{100} ???

- How many of these combinations will have the structure (crystallographic, nanoscale, microscale, etc.) of the end members?

- How is mixing them going to affect the resulting mechanical, electronic and other physical and chemical properties?

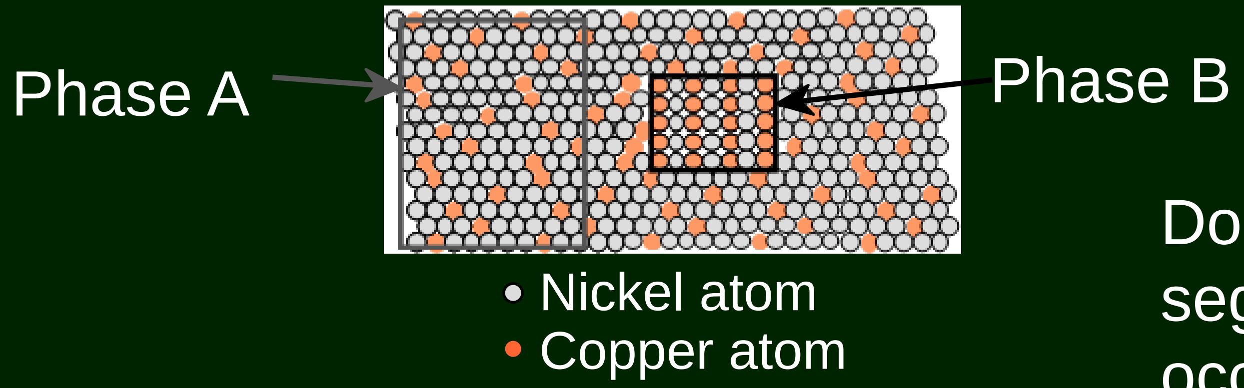
- Can the properties of the end members be improved on?

Phase Diagrams – Why?

- When we combine two or more constituents (elements)...
  what **equilibrium** state do we get?
- In particular, if we specify... *c*, *p*, *T*, but also *H*, *E*
  (all are intensive thermodynamic parameters)
  - composition (e.g., wt% Cu - wt% Ni), and
  - temperature (*T*)

then...

How many phases do we get?
What is the composition of each phase?
How much of each phase do we get?



Does this phase segregation really occur for $Cu_{1-x}Ni_x$?

Phase Equilibria: Solubility Limit

Introduction

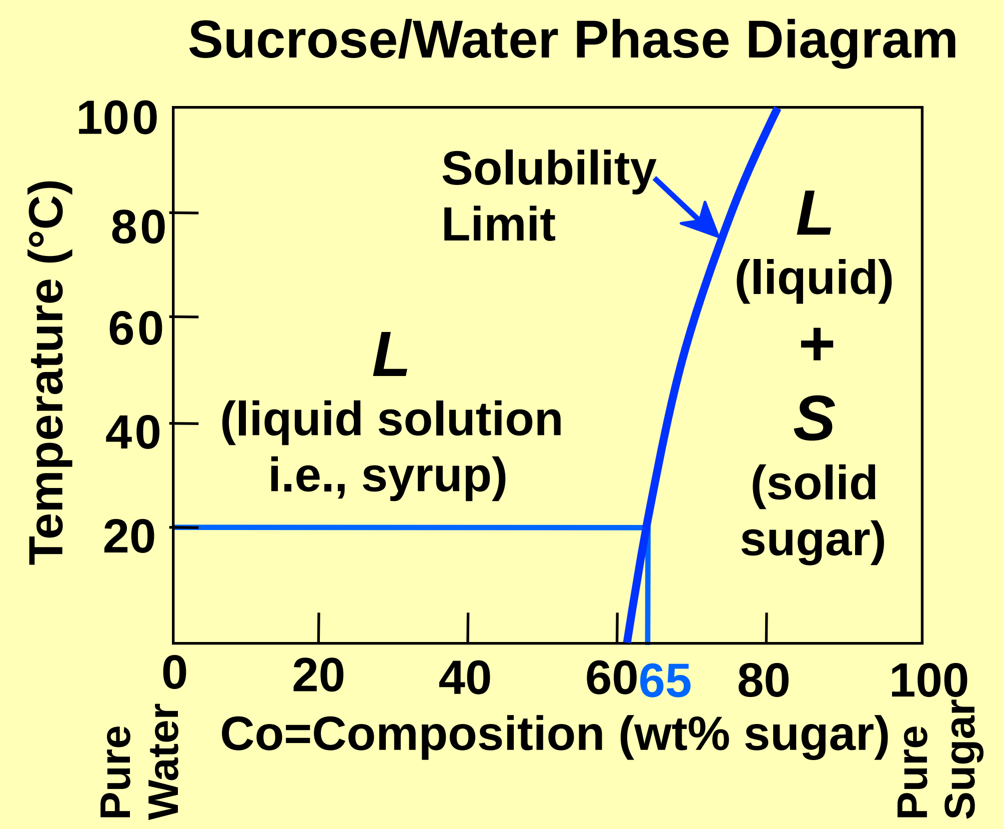
- Solutions – solid solutions, single phase
- Mixtures – more than one phase

- Solubility Limit:
  Max concentration for which only a single phase solution occurs.

Question: What is the solubility limit at 20°C?

Answer: 65 wt% sugar.

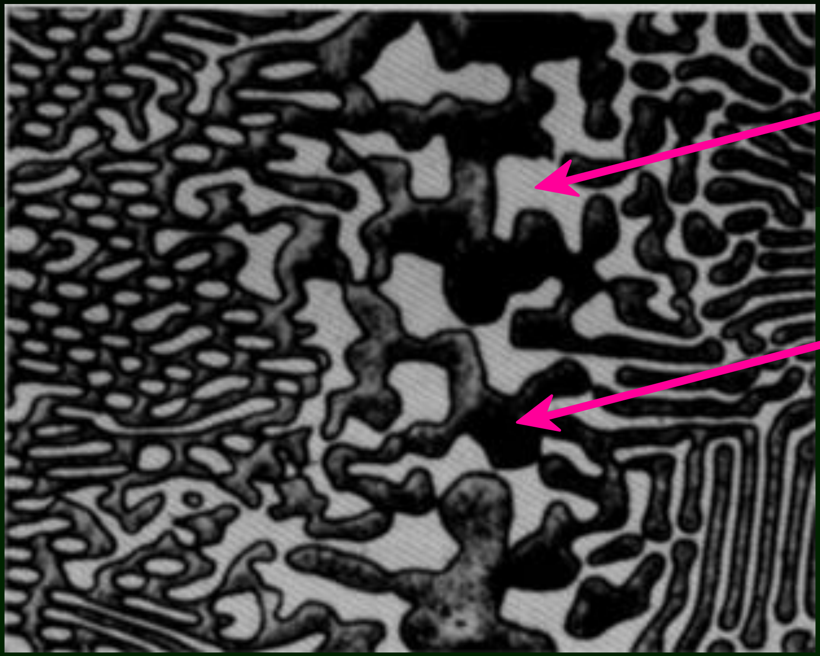
If C_O < 65 wt% sugar: syrup
If C_O > 65 wt% sugar: syrup + sugar.



Components and Phases

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

Aluminum-Copper Alloy



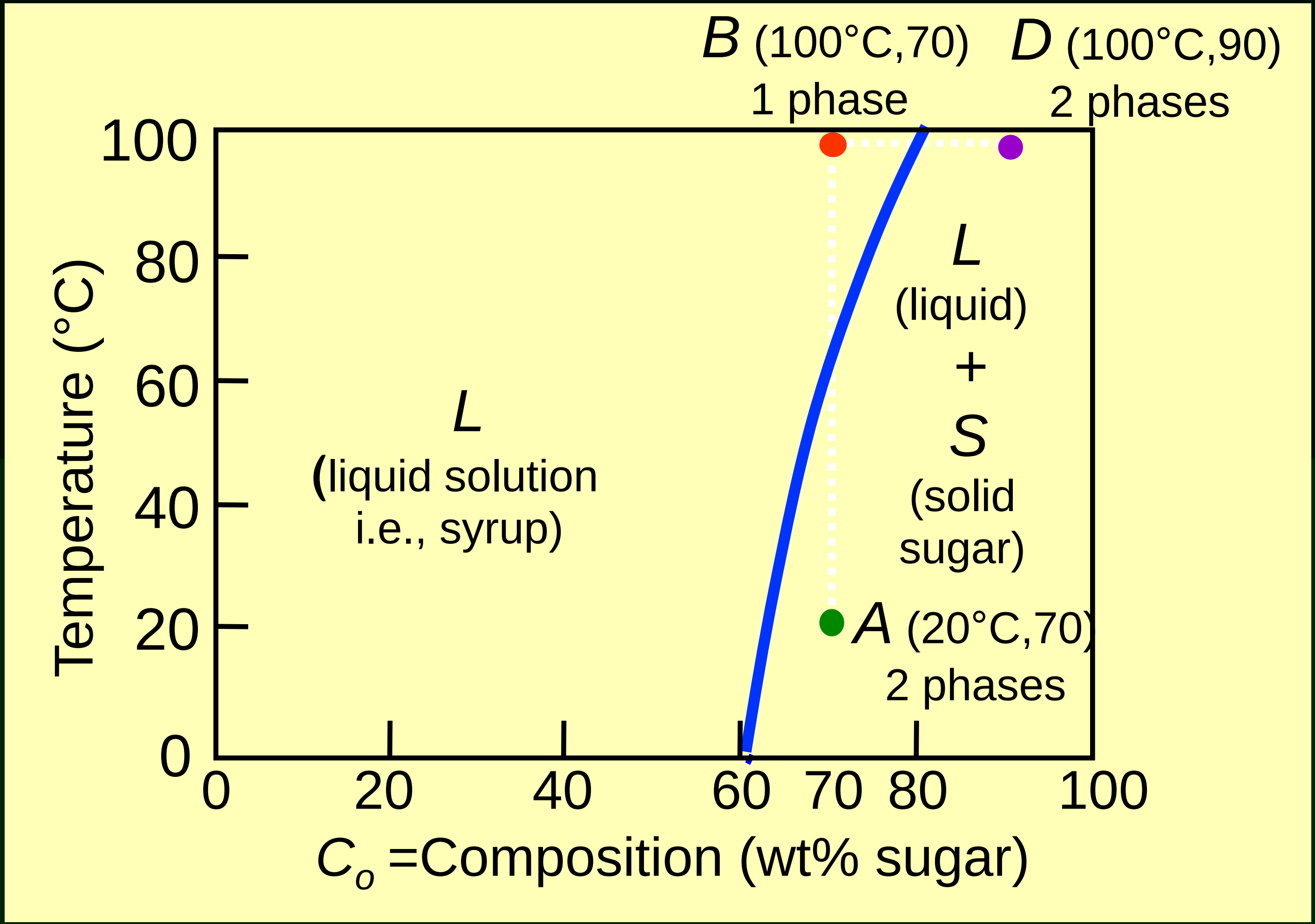
β (lighter phase)

α (darker phase)

Effect of *T* & Composition (C_o)

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

water-
sugar
system



Phase Equilibria

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

	Crystal Structure	Electroneg.	r (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

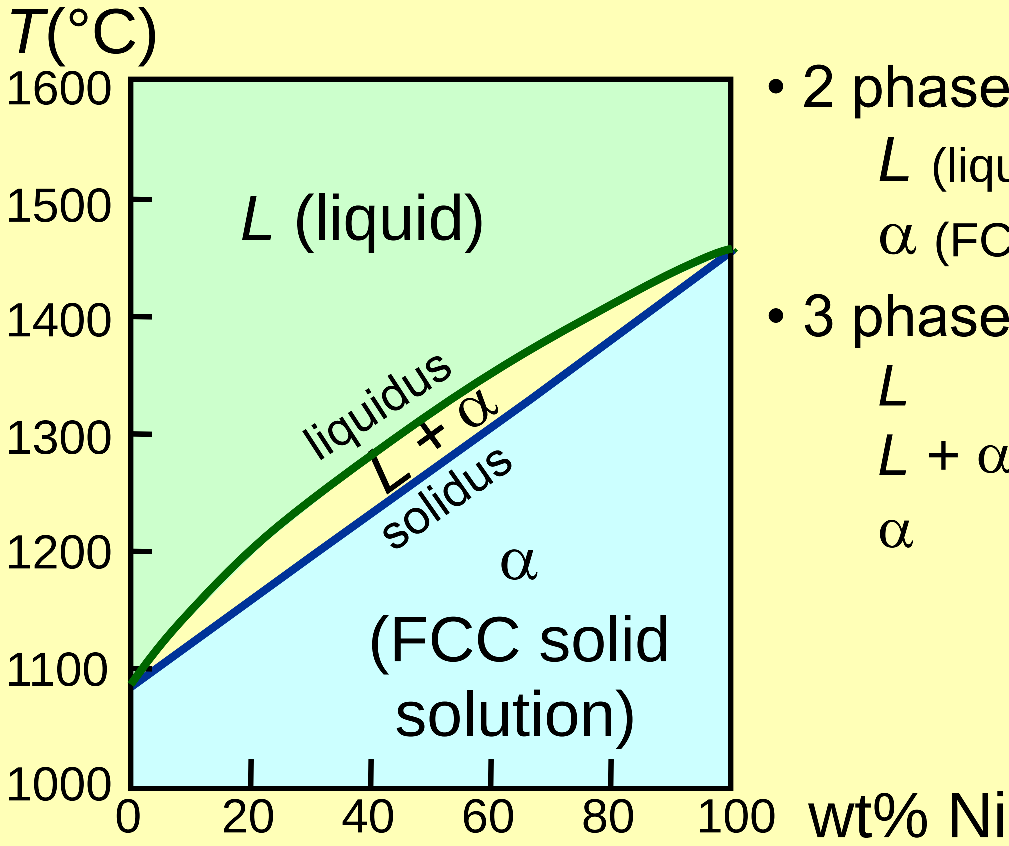
- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (*W. Hume – Rothery rules*) suggesting high mutual solubility.

- Ni and Cu are totally miscible in all proportions. Hence, the answer to the earlier question…is No…

Phase Diagrams

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

- Phase Diagram for Cu-Ni system



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

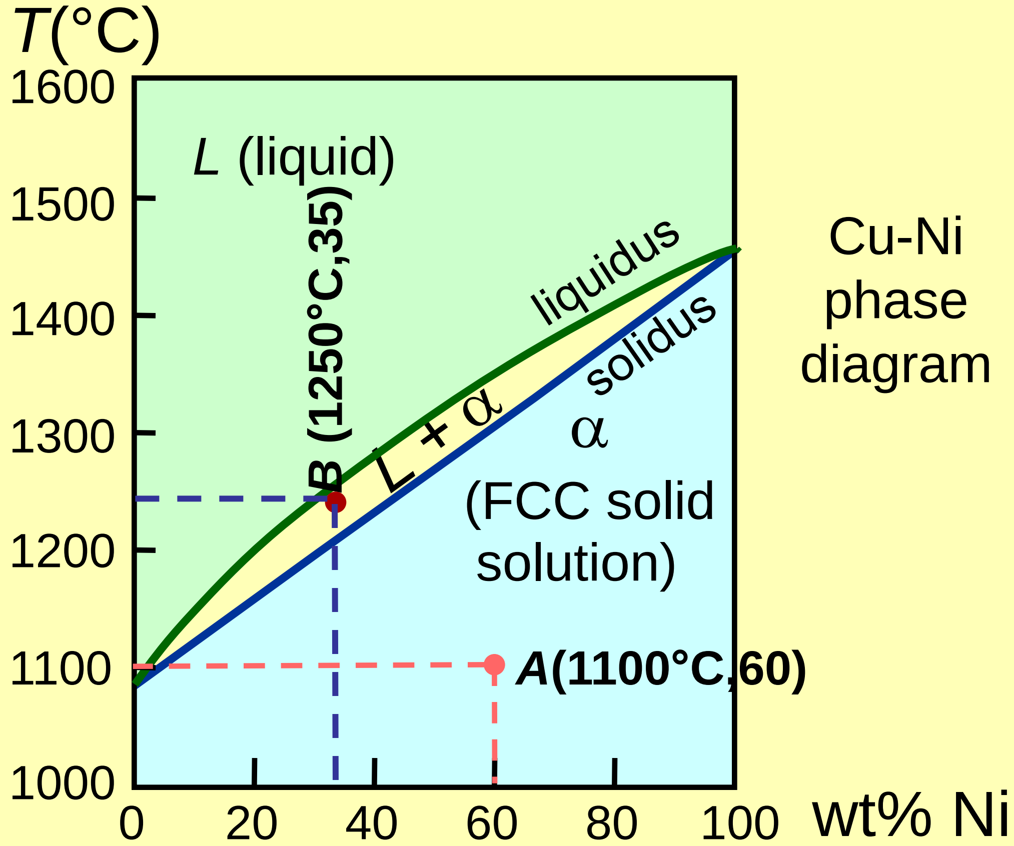
Phase Diagrams:
Number and types of phases

- Rule 1: If we know T and C_o, then we know:
  - the number and types of phases present.

- Examples:

  A(1100°C, 60):
  1 phase: α

  B(1250°C, 35):
  2 phases: *L* + α



Composition of phases

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

- Examples:

C_o = 35 wt% Ni

At T_A = 1320°C:

Only Liquid (L)

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

At T_D = 1190°C:

Only Solid (α)

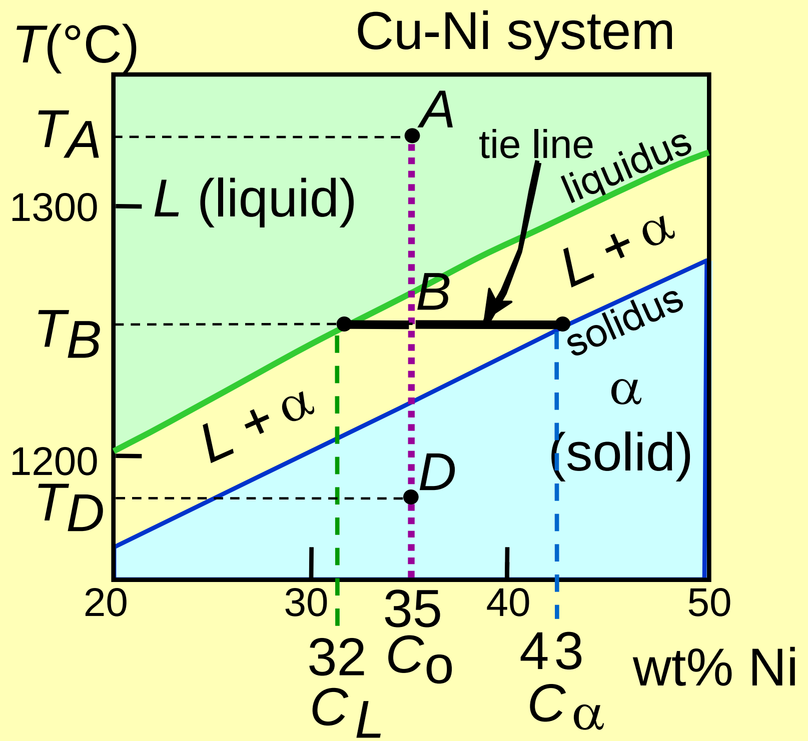
$C_\alpha = C_o$ (= 35 wt% Ni)

At T_B = 1250°C:

Both α and L

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

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



Weight fractions of phases

- Rule 3: If we know T and C_o, then we know:
  - the amount of each phase (given in wt%), via the so-called:
    'centre of gravity principle' or the 'lever rule'…
- Examples:

C_o = 35 wt% Ni

At T_A: Only Liquid (L)

W_L = 100 wt%, W_α = 0

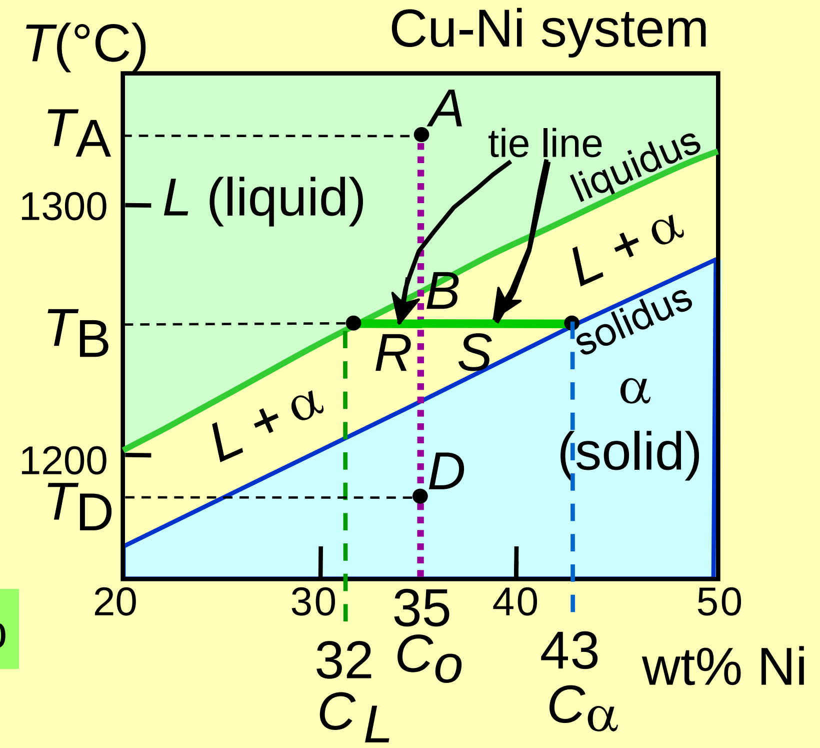
At T_D: Only Solid (α)

W_L = 0, W_α = 100 wt%

At T_B: Both α and L

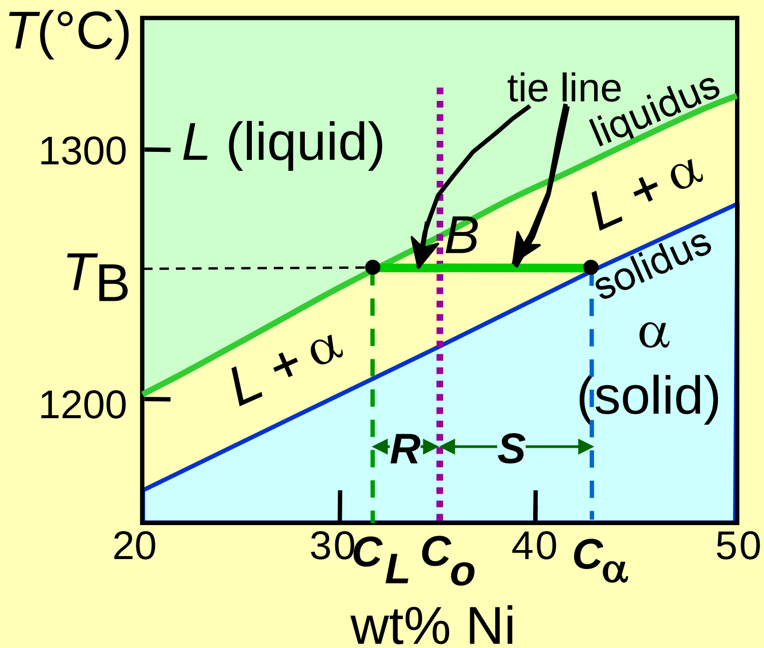
$$W_L = \frac{S}{R+S} = \frac{43-35}{43-32} = 73\,wt\%$$

$$W_\alpha = \frac{R}{R+S} = 27\text{ wt\%}$$

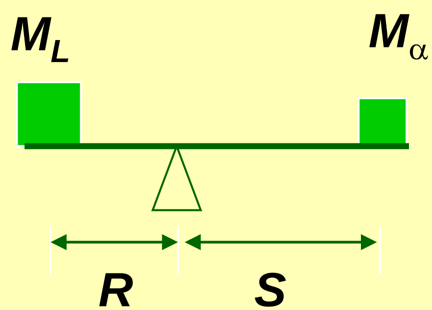


The Lever Rule

- Tie line – connects the phases in equilibrium with each other - essentially an isotherm



How much of each phase?
Think of it as a lever



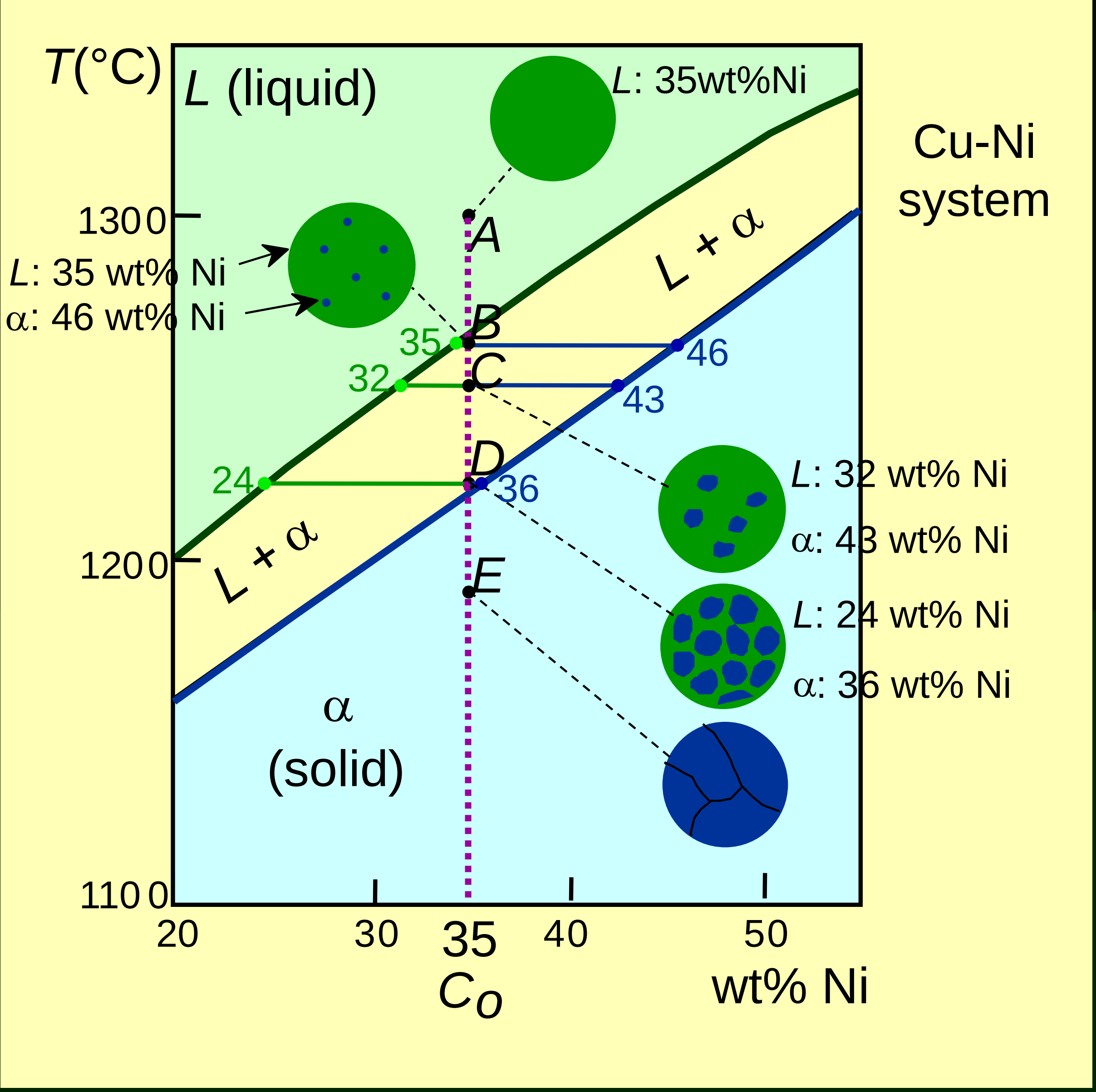
$$M_\alpha \cdot S = M_L \cdot R$$

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

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

Cooling in the Cu-Ni Binary System

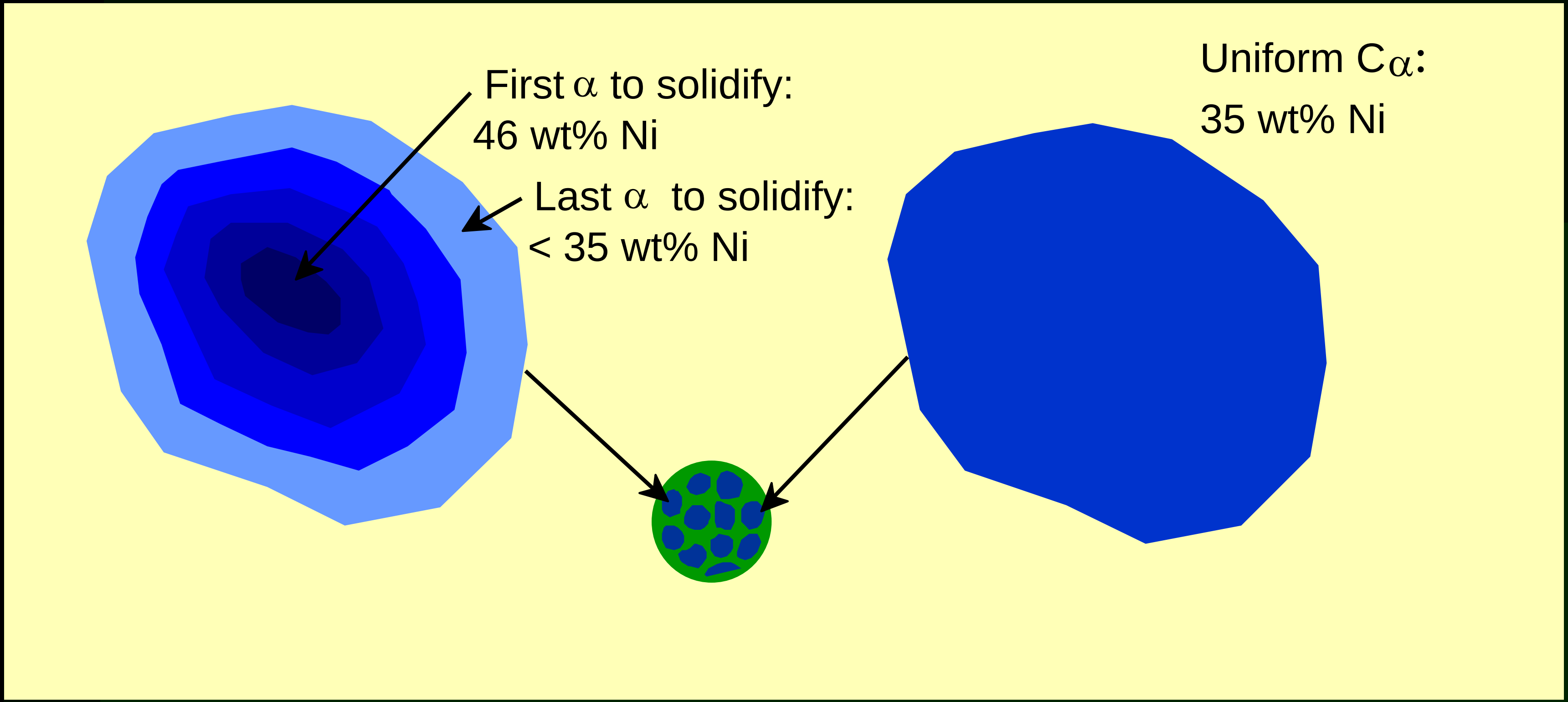
- Phase diagram:
  Cu-Ni system.
- System is:
  - binary
    i.e., 2 components:
    Cu and Ni.
  - isomorphous
    i.e., complete
    solubility of one
    component in
    another; α phase
    field extends from
    0 to 100 wt% Ni.
- Consider
  C_o = 35 wt%Ni.



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.

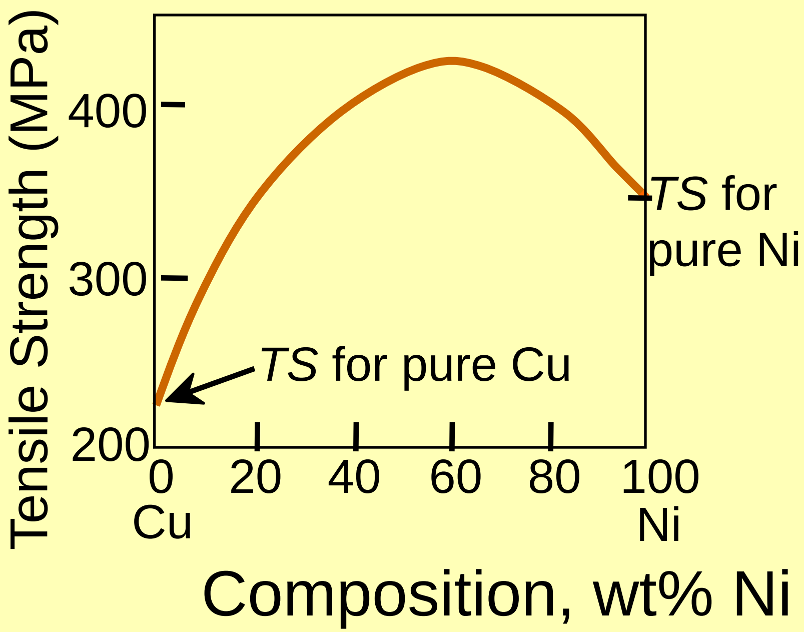
- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure

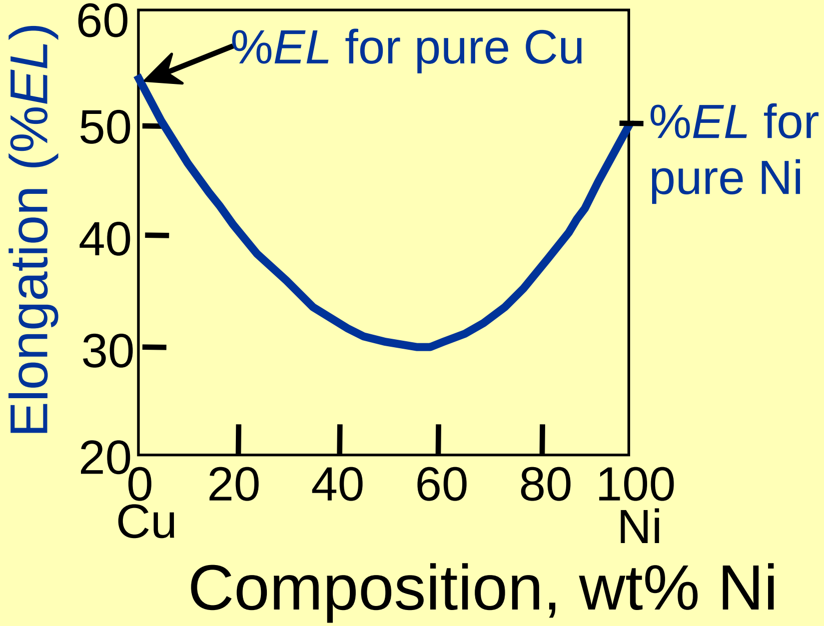


Mechanical Properties: Cu-Ni System

- Effect of solid solution strengthening on:

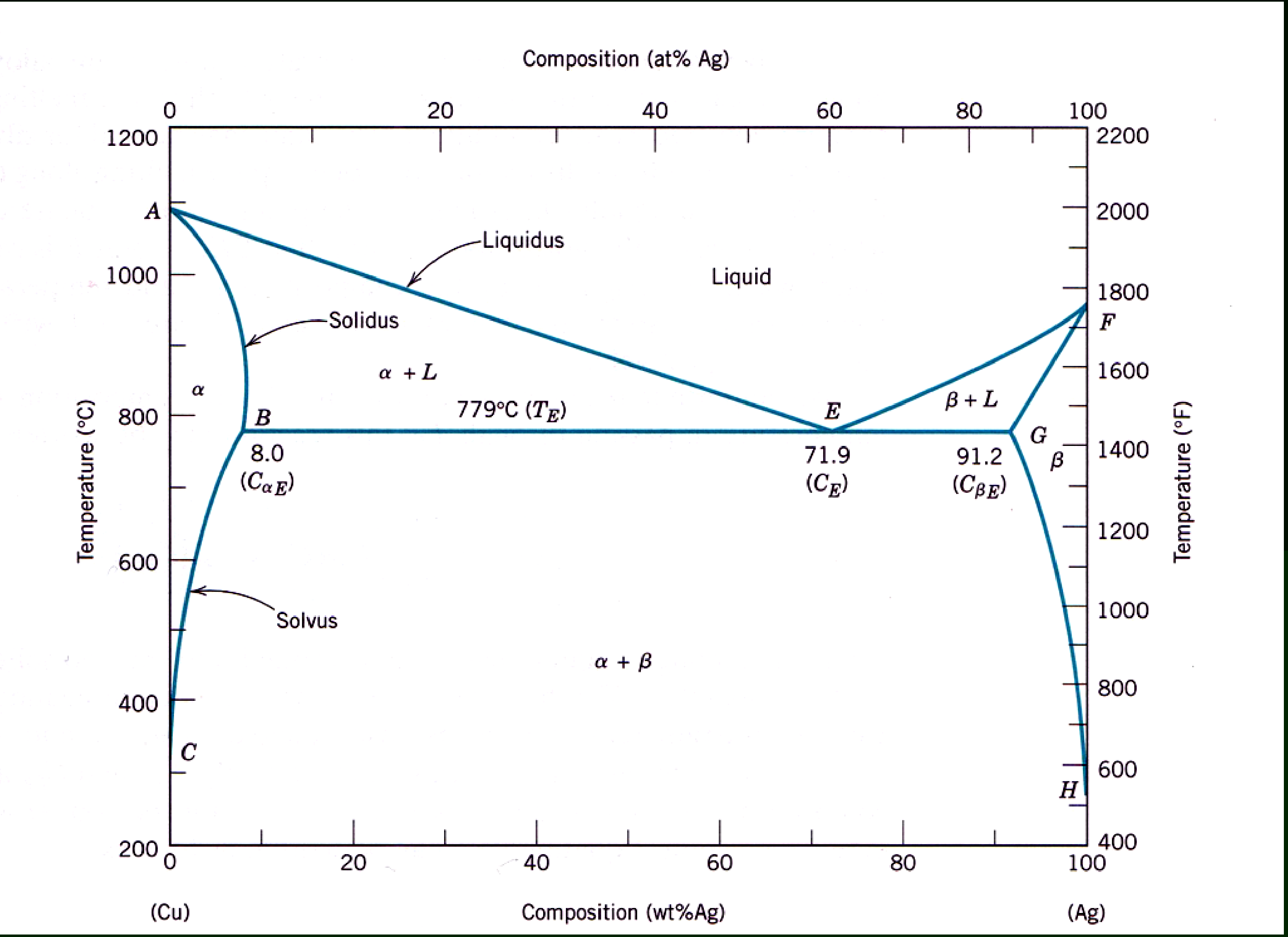
  - Tensile strength (*TS*)
  - Ductility (%*EL*,%*AR*)





- Maximum as a function of C_o
- Minimum as a function of C_o

Binary Eutectic Systems

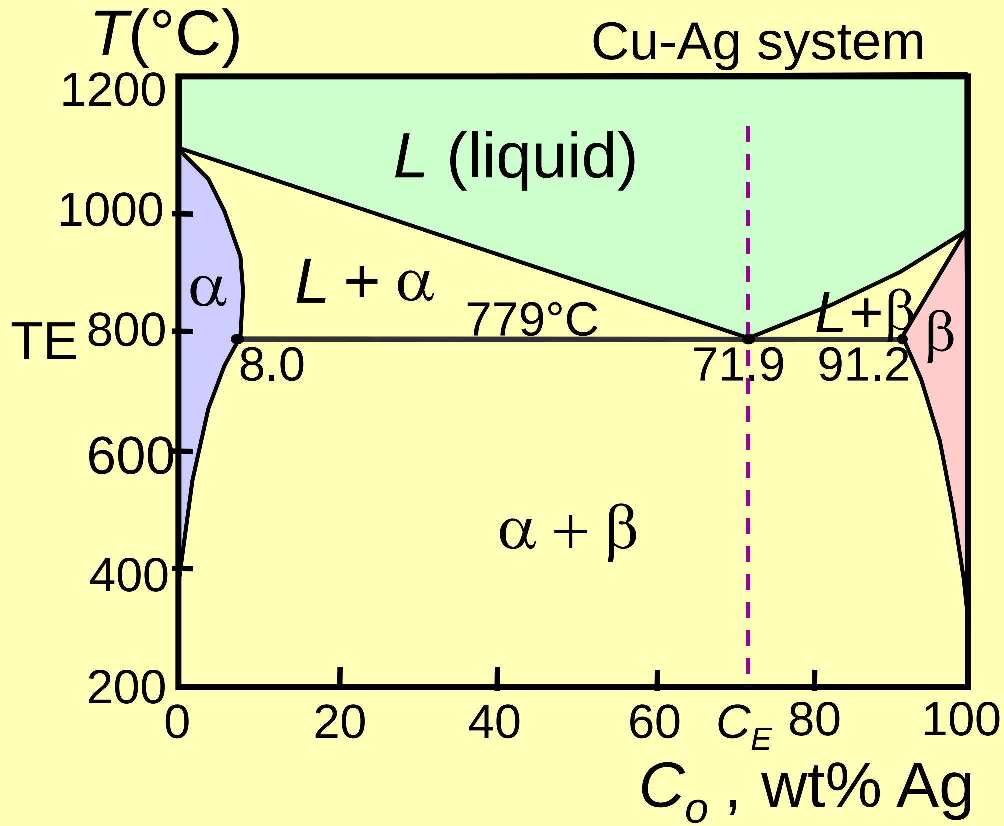


ευτηκτικός - from Greek 'easiest to melt'

Binary-Eutectic Systems

Cu-Ag system

- 3 single phase regions (L, α, β)
- Limited solubility:)
  α: mostly Cu
  β: mostly Ag
- T_E : No liquid below T_E
- C_E : Composition with min. melting T_E



- Eutectic transition

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$

Pb-Sn Eutectic System (1)

- For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find...
  - the phases present:
  - compositions of phases:

C_O = 40 wt% Sn
C_α = 11 wt% Sn
C_β = 99 wt% Sn

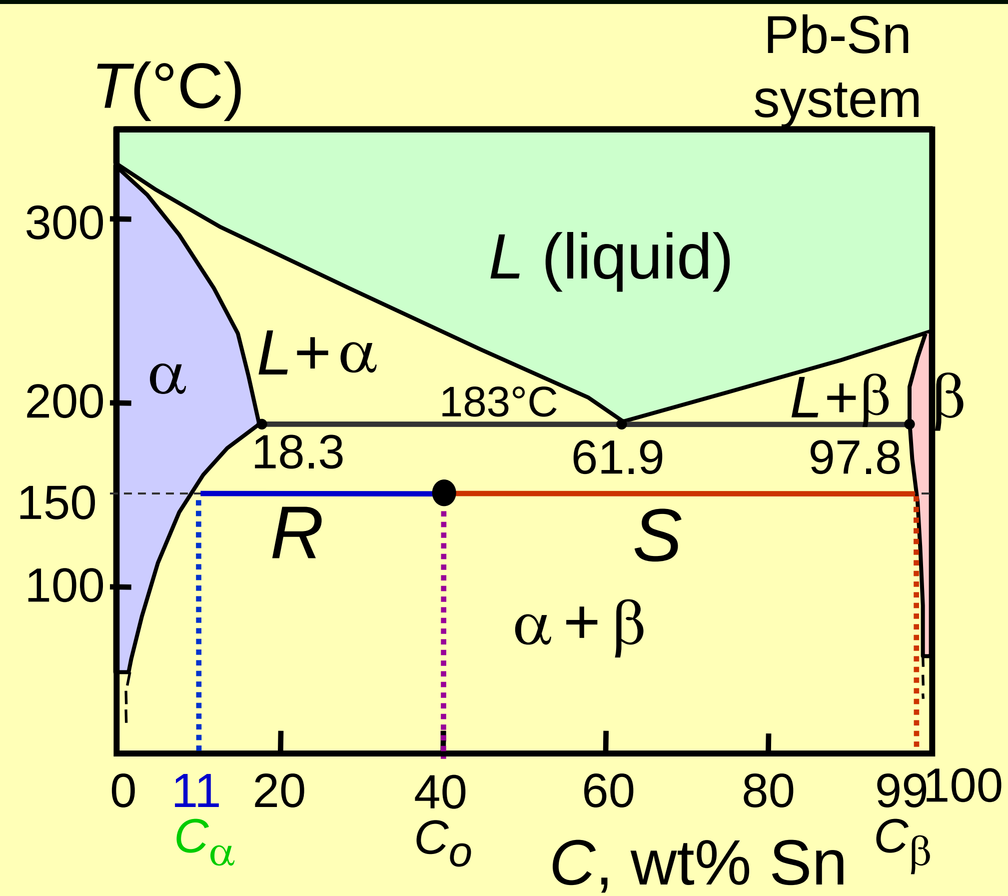
  - the relative amount of each phase:

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

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

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

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$



Adapted from Fig. 9.8, *Callister 7e.*

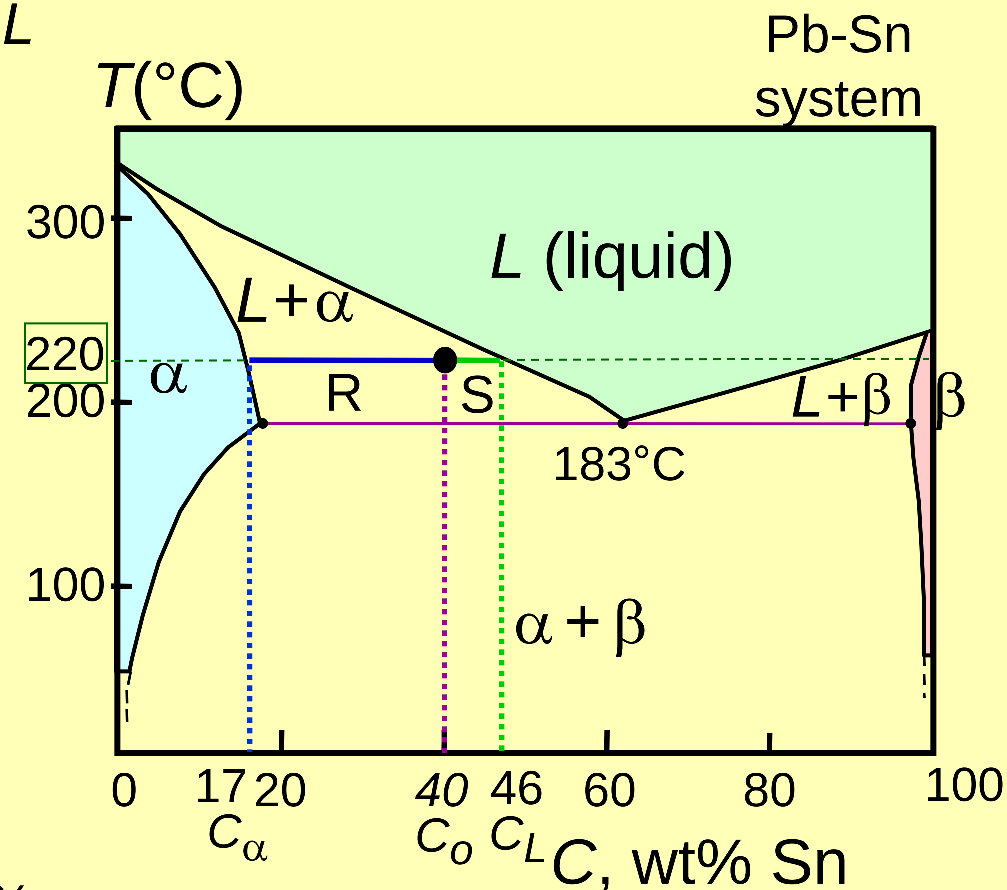
Pb-Sn Eutectic System (2)

- For a 40 wt% Sn-60 wt% Pb alloy at 220°C, find...
  - the phases present: $\alpha + L$
  - compositions of phases:

    C_O = 40 wt% Sn
    C_α = 17 wt% Sn
    C_L = 46 wt% Sn
  - the relative amount of each phase:

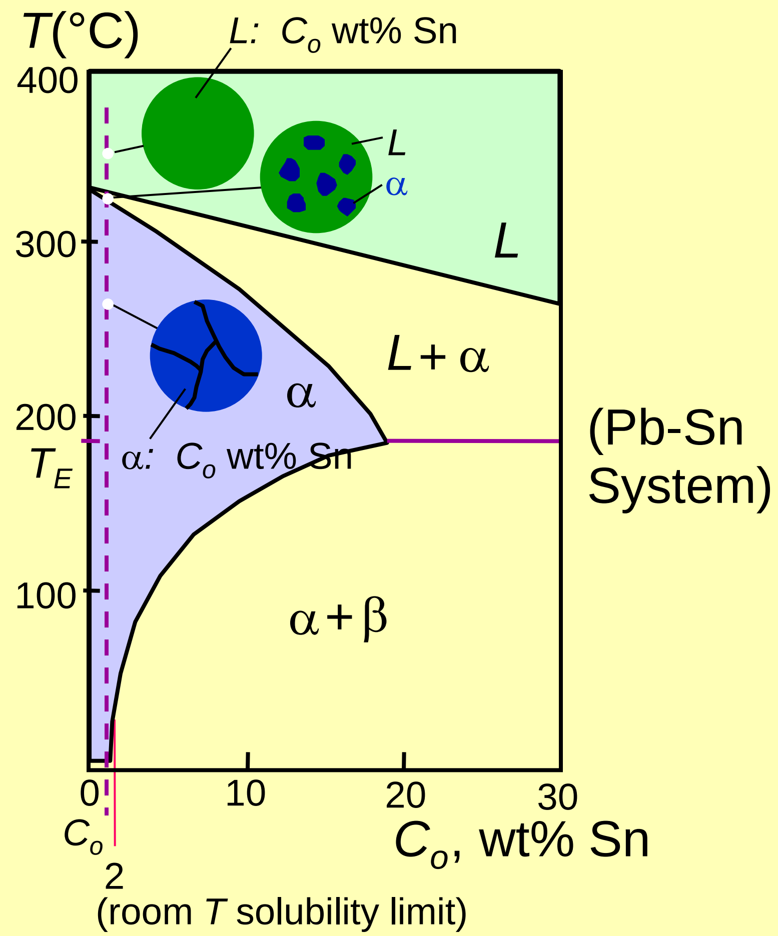
$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17} = \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$



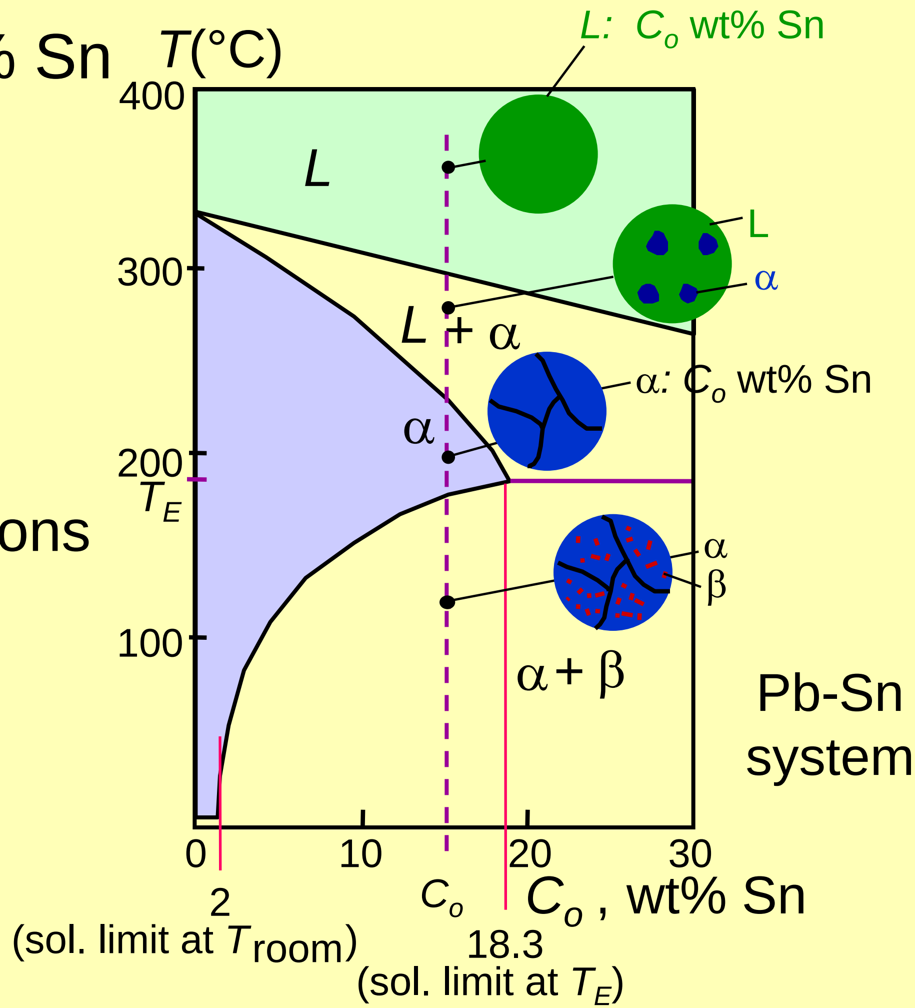
Microstructures in Eutectic Systems: I

- C_o < 2 wt% Sn
- Result:
  - at extreme ends
  - polycrystal of α grains
    i.e., only one solid phase.



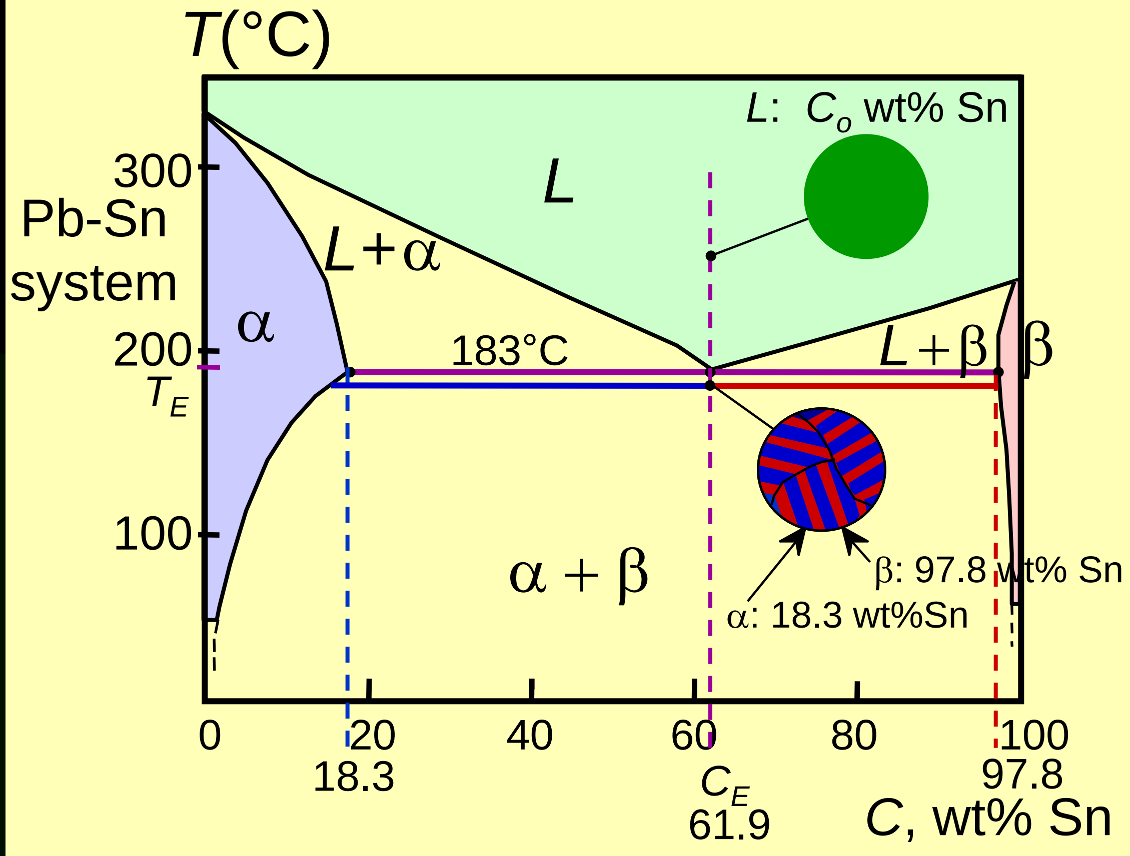
Microstructures in Eutectic Systems: II

- 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - Initially liquid + α
  - then α alone
  - finally two phases
    - α polycrystal
    - fine β-phase inclusions

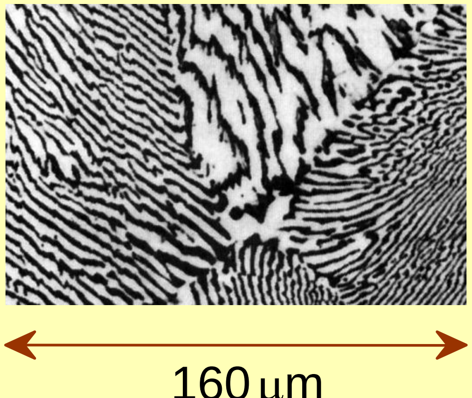


Microstructures in Eutectic Systems: III

- $C_o = C_E$
- Result: Eutectic microstructure (lamellar structure)
  - alternating layers (lamellae) of α and β crystals.

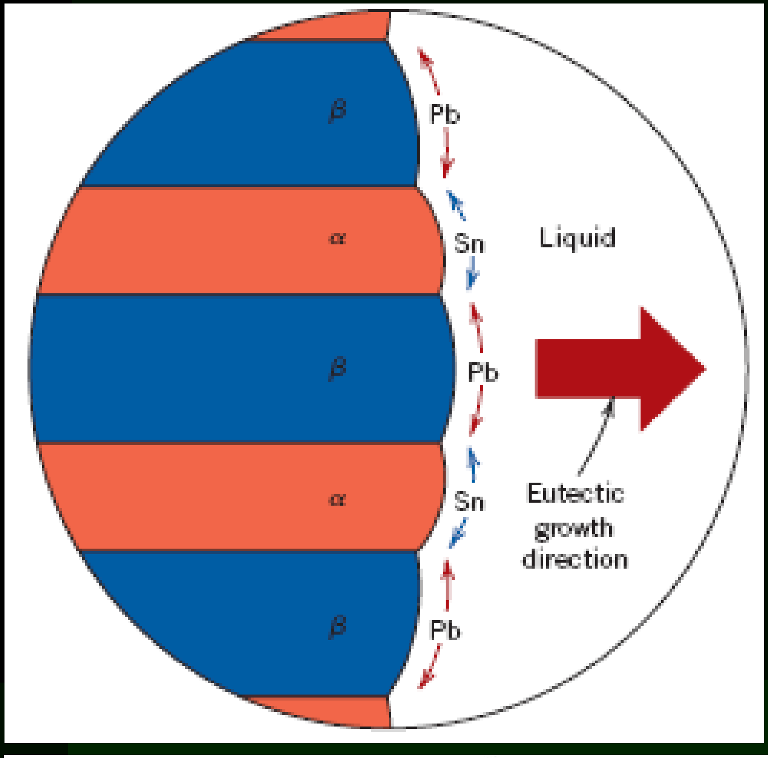


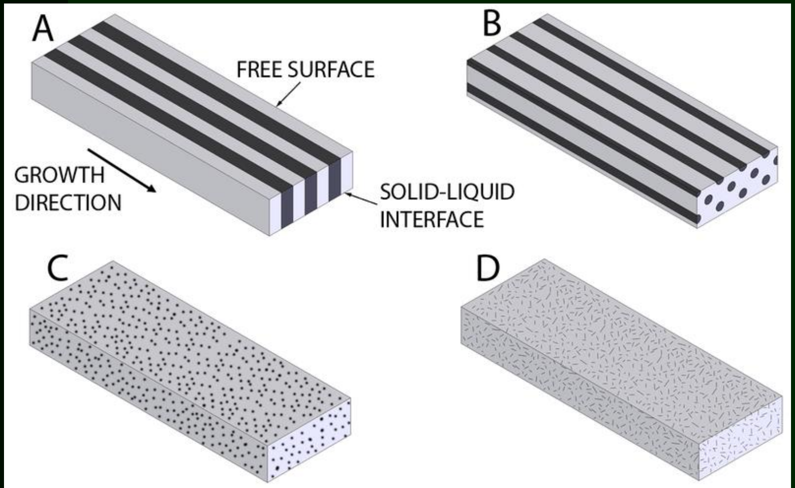
Micrograph of Pb-Sn eutectic microstructure

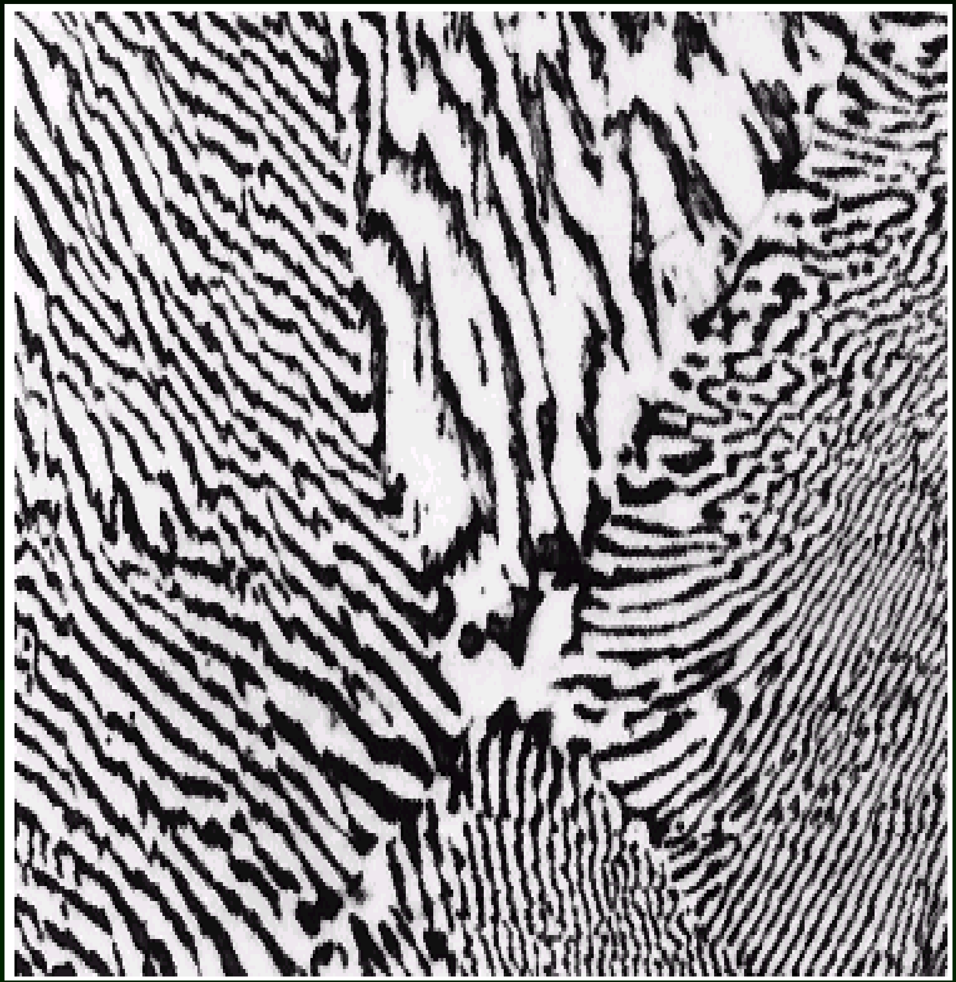


Adapted from Fig. 9.14, *Callister 7e.*

Lamellar Eutectic Structure



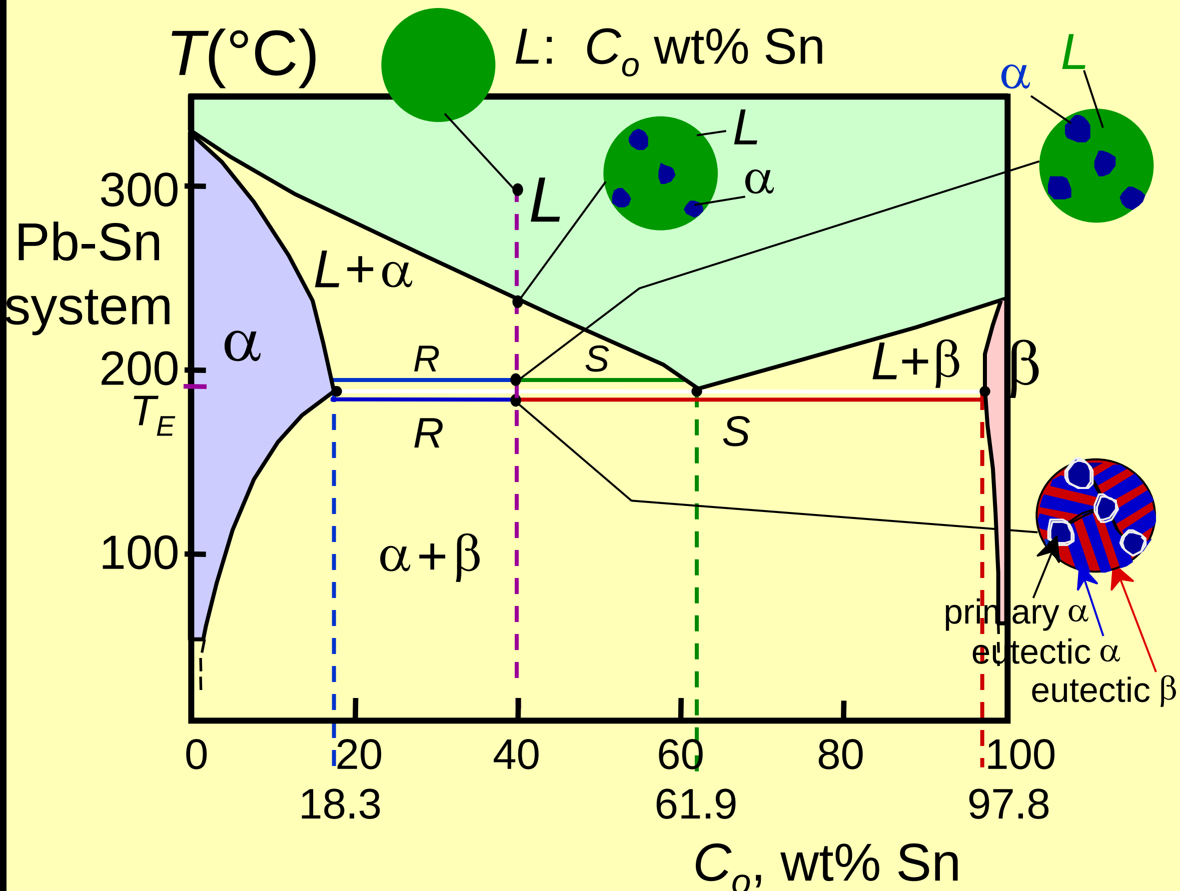




← Other possible eutectic structures are: rod-like, globular and acicular.

Microstructures in Eutectic Systems: IV

- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- Result: α crystals and an eutectic microstructure



- Just above T_E:

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 50 \text{ wt\%}$$

$W_L = (1 - W_\alpha) = 50$ wt%

- Just below T_E:

C_α = 18.3 wt% Sn

C_β = 97.8 wt% Sn

$$W_\alpha = \frac{S}{R+S} = 73 \text{ wt\%}$$

W_β = 27 wt%