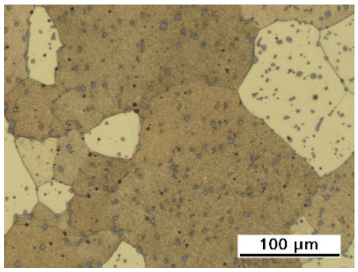
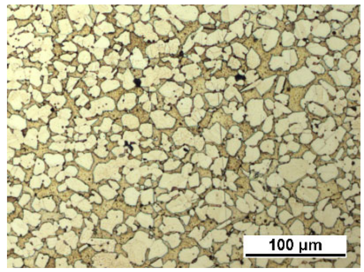
Phase diagrams

41680 Introduction to advanced materials





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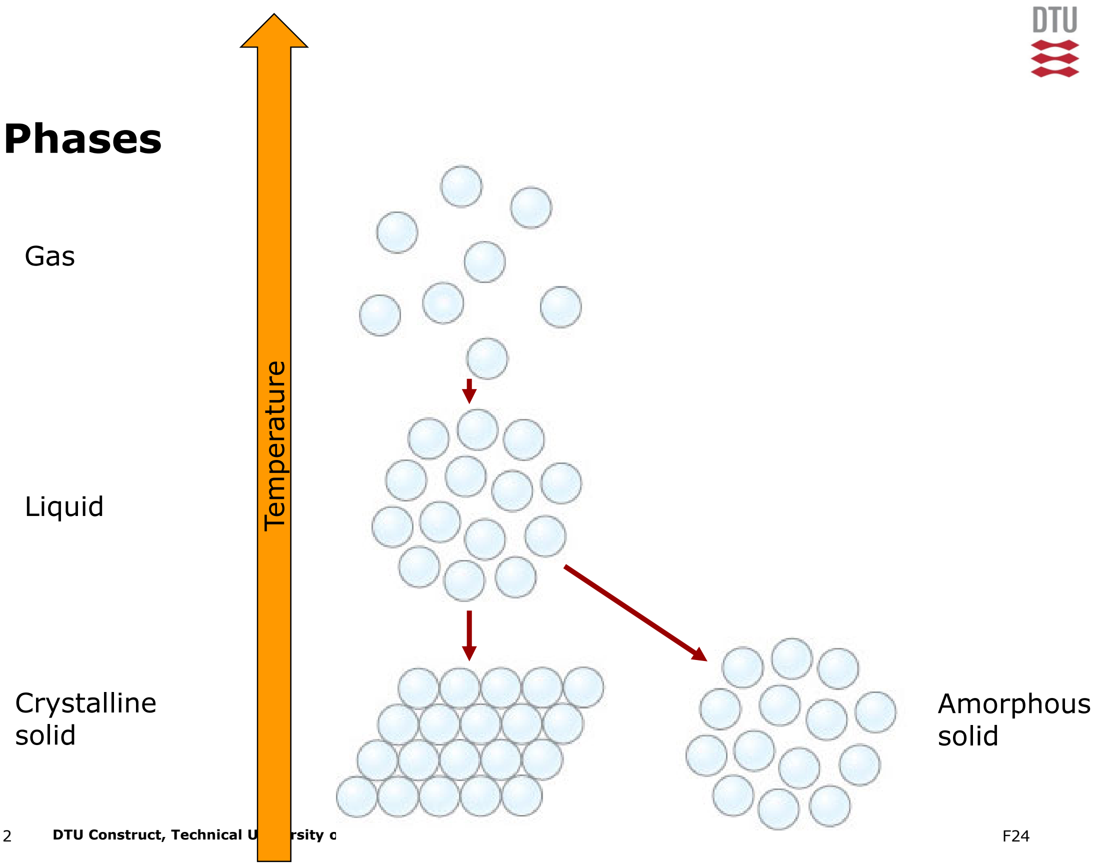
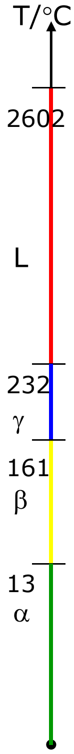
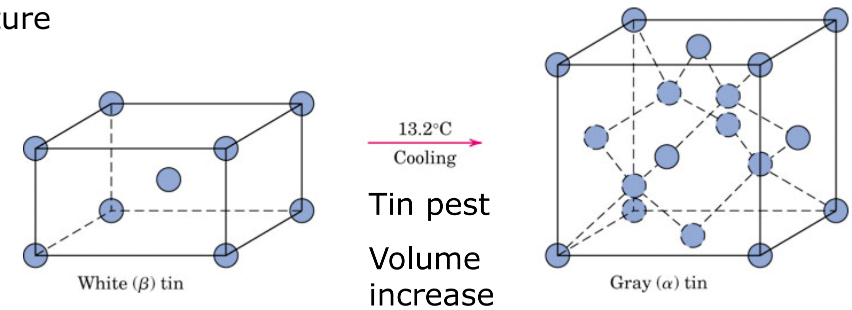
Phases





Allotropy of elements: tin

- 50 electrons, electron configuration [Kr] $4d^{10}$ $5s^2$ $5p^2$
- 4 valence electrons = 4 atomic bonds
- 3 different (allotrope) structures
- γ Sn: rhombic
- β Sn (white Sn): metallic, tetragonal
- α Sn (grey Sn): nonmetallic, diamond structure



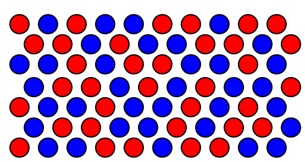
Tin pest

Volume increase 27%

diamond structure

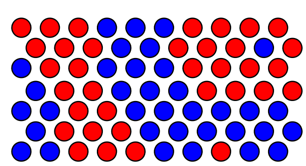
Alloys – three principle types

- Solid solutions = foreign atoms in crystal lattice



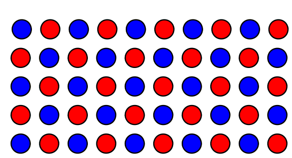
- Atoms unordered in same lattice

- Mixture of different metallic phases



- Distinct phases with different composition and possibly different lattices

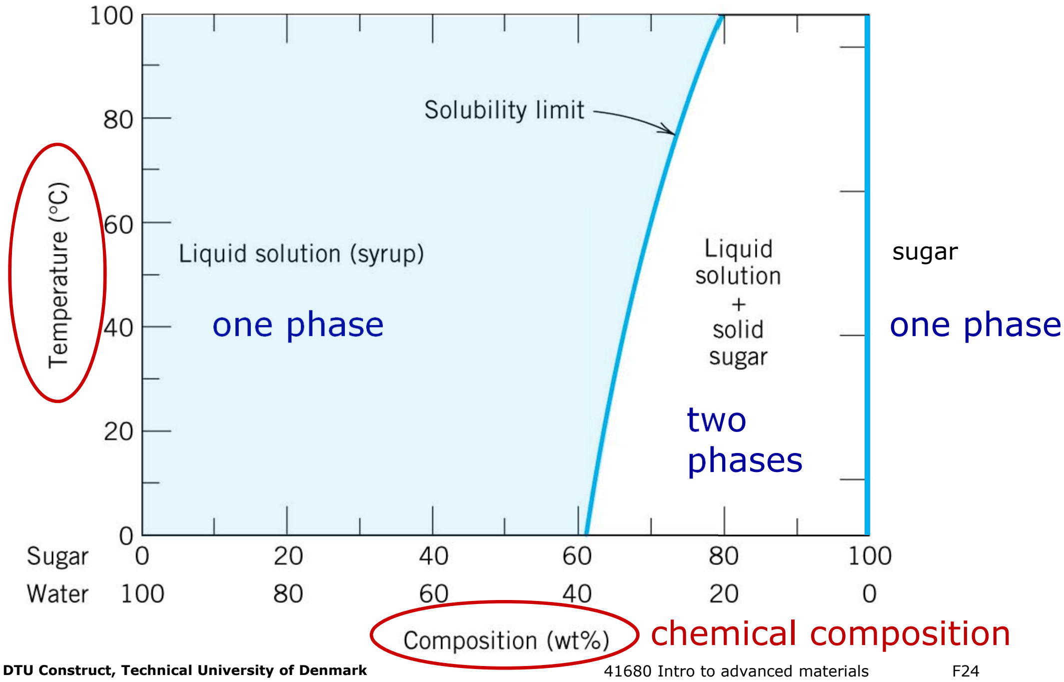
- Intermetallic compounds



- Atoms ordered in possibly different lattice

Which version exists is seen in phase diagrams!

Phases and solubility
Example: sugar – water system
Binary system (two components)



Phases and solubility

Phase

- Definition: Homogeneous part of a system, i.e. equal (unique) chemical and physical properties
- Characteristic parts of a heterogeneous system

Examples

- Gas, Liquid, Solid -> Ice water (as two phase system)
- Single phase materials
- Several solid phases (allotropy, polymorphism) α- and β-tin, α-Fe (bcc) and γ-Fe (fcc)

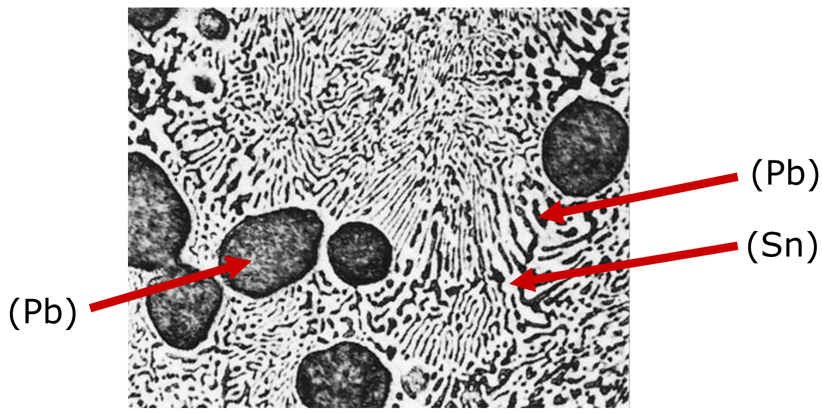
Solubility limit

- Maximum concentration of A (e.g. sugar) in B (e.g. water)

Material properties depend on:

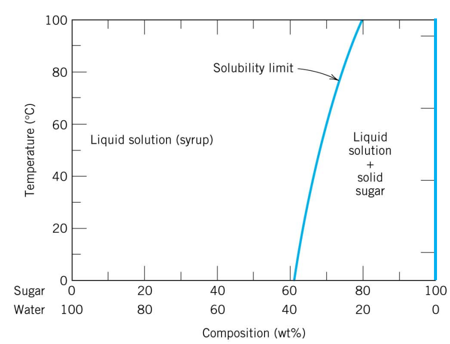
- Number of phases
- Chemical composition and crystal structure of each phase
- Phase fraction (mass or volume fraction)
- Size and spatial arrangement of phases

Example Pb-Sn



Phase diagrams

Graphical representation of phases as function of temperature and chemical composition



Equilibrium phase diagrams

😐 represent state of lowest energy (Gibbs energy *G*)

☺ show phases in equilibrium

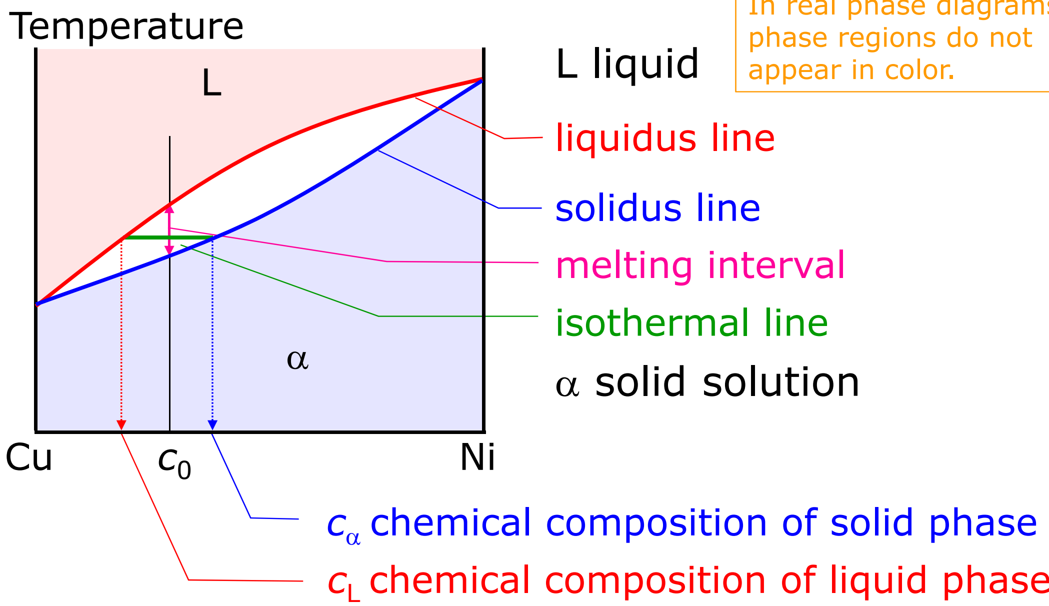
☹ do not show how much time is required for attaining equilibrium

Metastable state (non-equilibrium)

sometimes equilibrium never obtained (for assessable time)

Isomorphous binary phase diagram
Complete solubility in solid an liquid state

In real phase diagrams, phase regions do not appear in color.



c_0 chemical composition of alloy

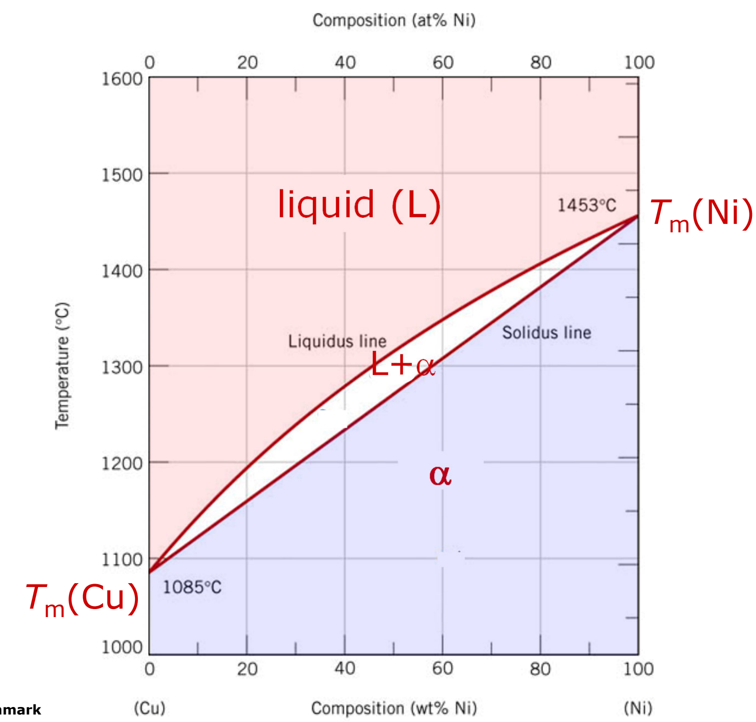
Isomorphous binary phase diagram
Example Cu-Ni

2 phases
- liquid (L)
- solid phase (α)

3 regions
- L
- L + α
- α

liquidus line

solidus line

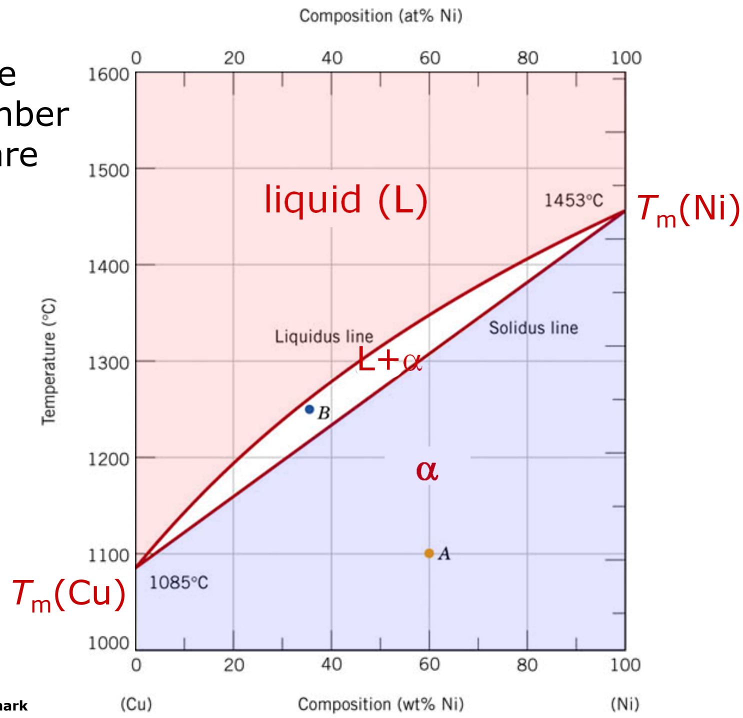


Isomorphous binary phase diagram

Example Cu-Ni

- For given temperature and composition, number and existing phases are revealed

- Examples
- A T = 1100 °C
  c_0 = 60 wt.% Ni
  ⇒ α
- B T = 1250 °C
  c_0 = 35 wt.% Ni
  ⇒ α + L



Isomorphous binary phase diagram

Composition c of phases

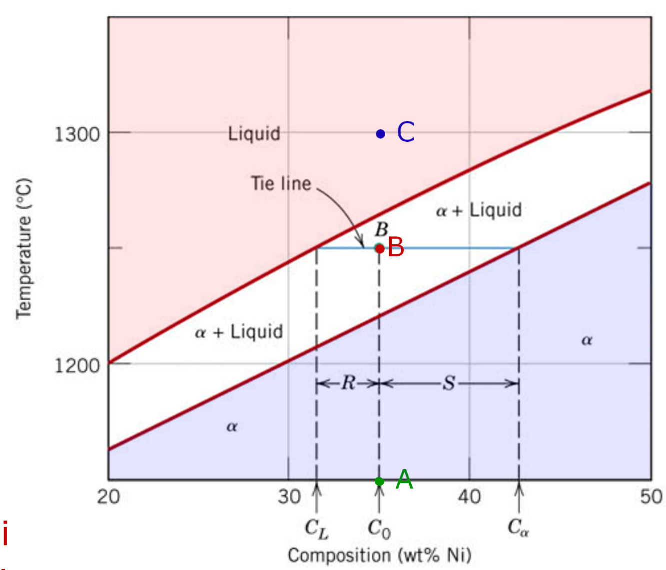
Cu-Ni system

c_0 = 35 wt.% Ni

C: at T = 1300°C
→ L (liquid)
⇒ c_0 = c_L= 35 wt.% Ni

A: at T = 1150°C
→ α (solid)
⇒ c_0 = c_α = 35 wt.% Ni

B: at T = 1250 °C
→ L + α
⇒ c_L = c_{liq} = 32 wt.% Ni
c_α = c_{sol}= 43 wt.% Ni



Lever rule for mass fractions
(weight fractions)

- Sum of mass fractions

$$1 = W_\alpha + W_L$$

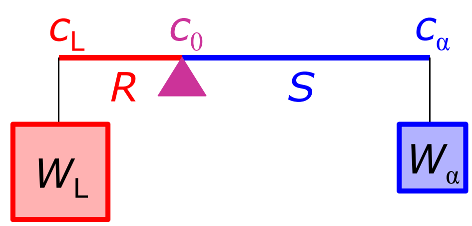
- Average composition (conservation of mass)

$$c_0 = c_\alpha W_\alpha + c_L W_L$$

- Combination (lever rule)

$$W_\alpha = \frac{c_0 - c_L}{c_\alpha - c_L} = \frac{R}{S+R} \qquad W_L = \frac{c_\alpha - c_0}{c_\alpha - c_L} = \frac{S}{S+R}$$

- Geometrical analogy



- Balance of torques

$$W_L R = W_\alpha S$$

Isomorphous binary phase diagram
Mass fractions *W* of individual phases

Cu-Ni system

c_0 = 35 wt.% Ni

B: T = 1250 °C

$\rightarrow$ L + α

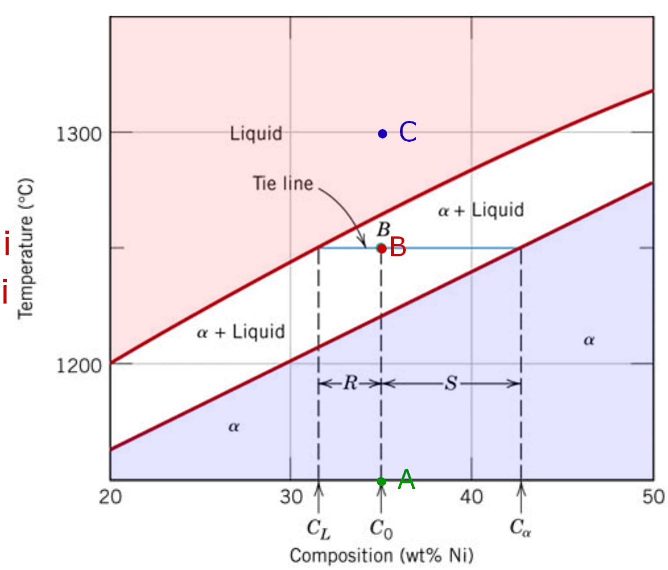
$\Rightarrow c_L = c_{liq}$ = 32 wt.% Ni

$c_\alpha = c_{sol}$ = 43 wt.% Ni

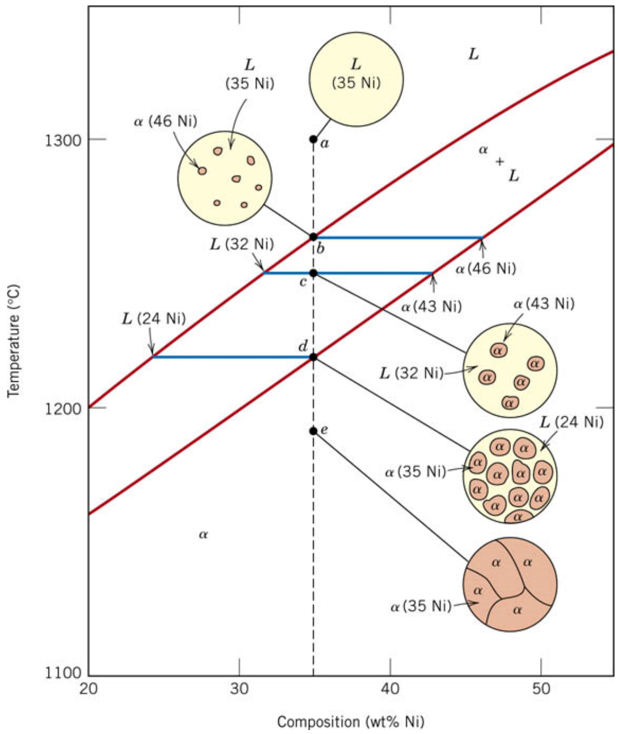
$$\boxed{W_L = \frac{c_\alpha - c_0}{c_\alpha - c_L}} = \frac{43-35}{43-32} = 73\ \%$$

$$\boxed{W_\alpha = \frac{c_0 - c_L}{c_\alpha - c_L}} = \frac{35-32}{43-32} = 27\ \%$$

$$W_\alpha + W_L = 100\ \%$$



Microstructure – equilibrium cooling
Isomorphous binary system (complete solubility)

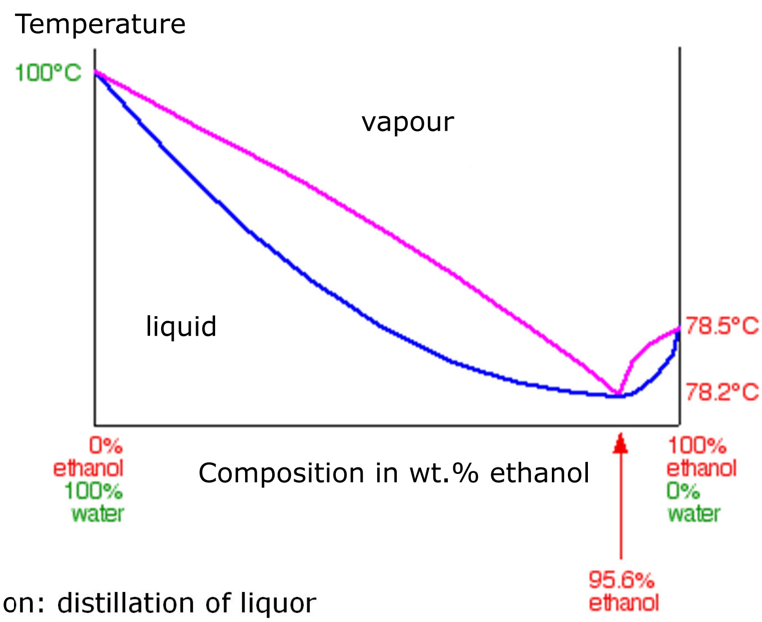


Equilibrium
i.e. extremely slow cooling

During solidification
change of composition of phases by atomic motion (diffusion)

Diffusion
- depends on time and temperature
- faster at higher temperatures

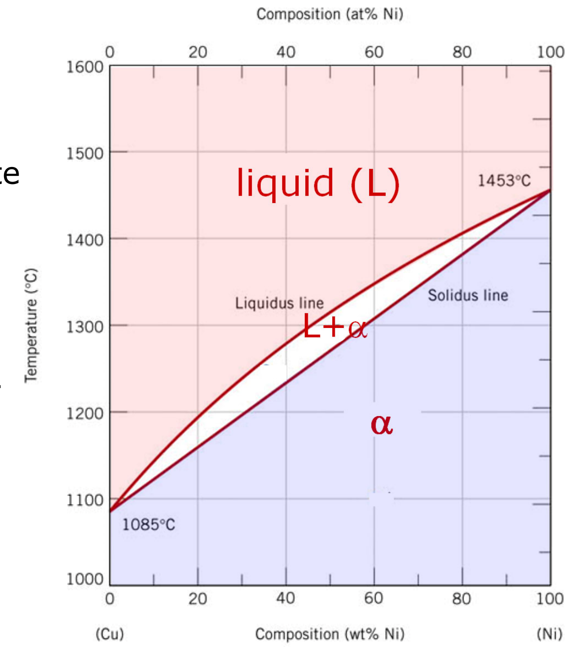
Phases and solubility
Example: ethanol – water system
Binary system (two components)



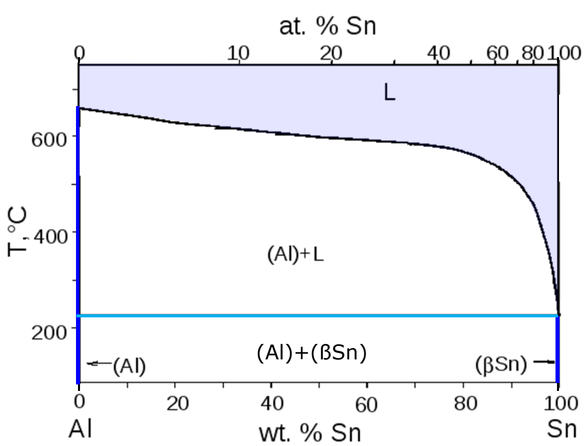
- Application: distillation of liquor

Isomorphous binary phase diagram

- Starting point: two different alloys of two components, Cu and Ni, which are completely solvable in each other in the liquid as well as the solid state
- Alloy A with 5 wt.% Ni
- Alloy B with 55 wt.% Ni
- Sketch the microstructure for both alloys after equilibrium cooling to room temperature
- Which phases are formed?



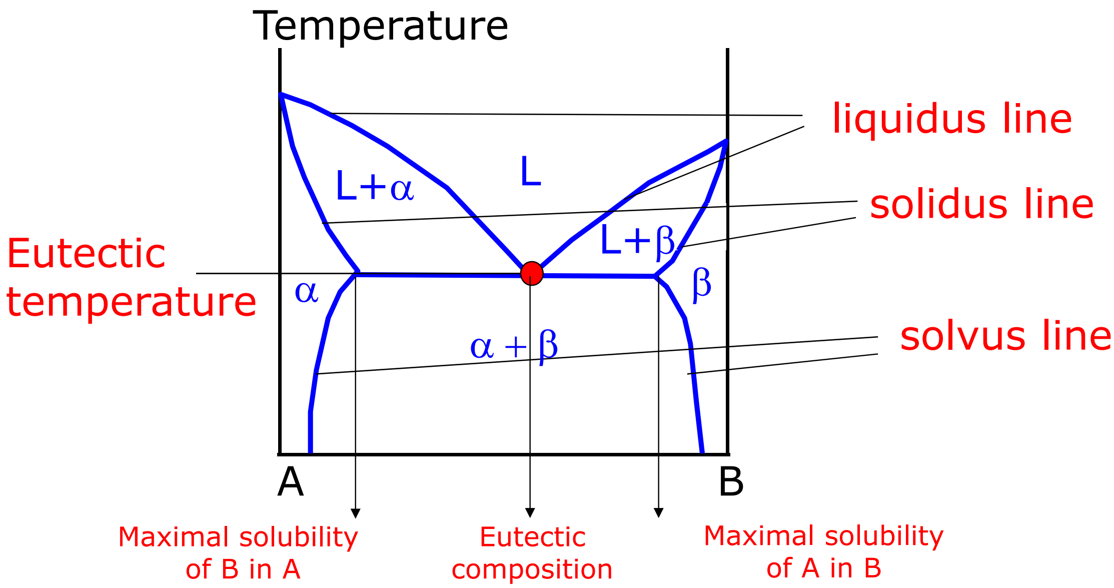
Binary system without any solubility
Example Al-Sn



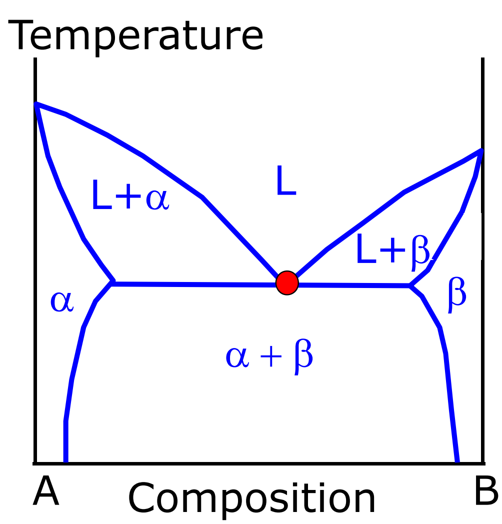
- Identify and mark
  - One phase regions (3)
  - Two phase regions (2)
  - Liquidus line
  - Solidus line
- A liquid with 40% wt. Sn is cooled from 700 °C under equilibrium conditions
  - At which temperature does solidification occur?
  - What is the first solid phase?
  - Which phases exist at 400 °C?
  - What is their composition?
  - Which phases exist at 200 °C?
  - What is their composition?

Binary eutectic systems

Limited solubility in the solid state



Gibbs phase rule



One phase region
neither *T*, nor *c* fixed

Two phase region
c (of phases) fixed,
T free

Three phase point
both *T* and *c* (of phases) fixed

1-2-1 rule
along isotherm

Number of degrees of freedom + Number of phases in equilibrium = Number of constituents + 1

Binary eutectic system

Example Cu-Ag

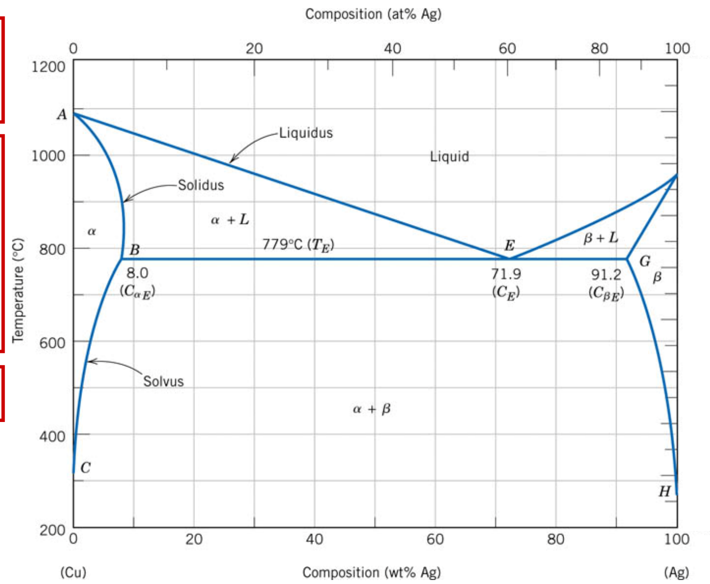
3 one phase regions (L, α, β)

Limited solubility
- of B in A
  α–solid solution
- of A in B
  β–solid solution

eutectic temperature

eutectic
hypo-eutectic (under)
hyper-eutectic (over)

liquidus line
solidus line
solvus line



Binary eutectic system

Example 33 wt.% Ag 67 wt.% Cu at 575 °C

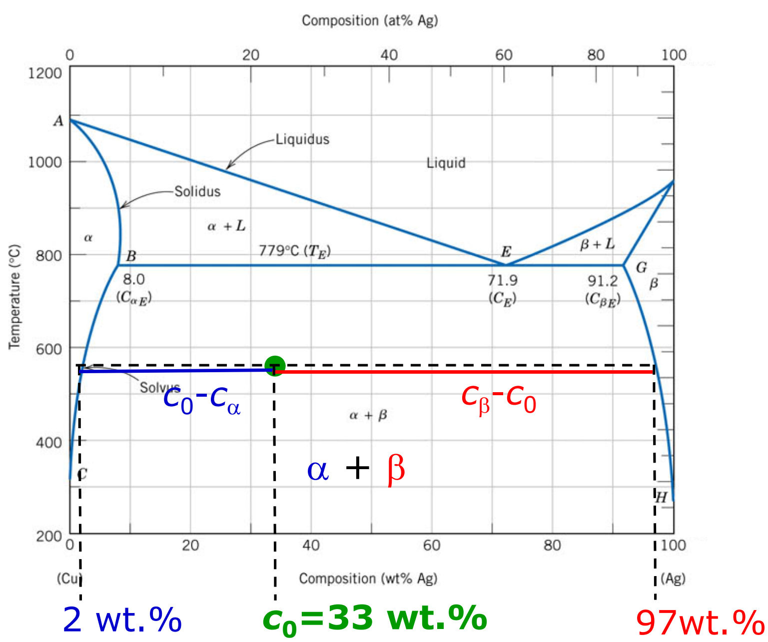
Phases present (2)
α and β

Phase compositon
c_α = 2 wt.% Ag
c_β = 97 wt.% Ag

Mass fraction of each phase from lever rule

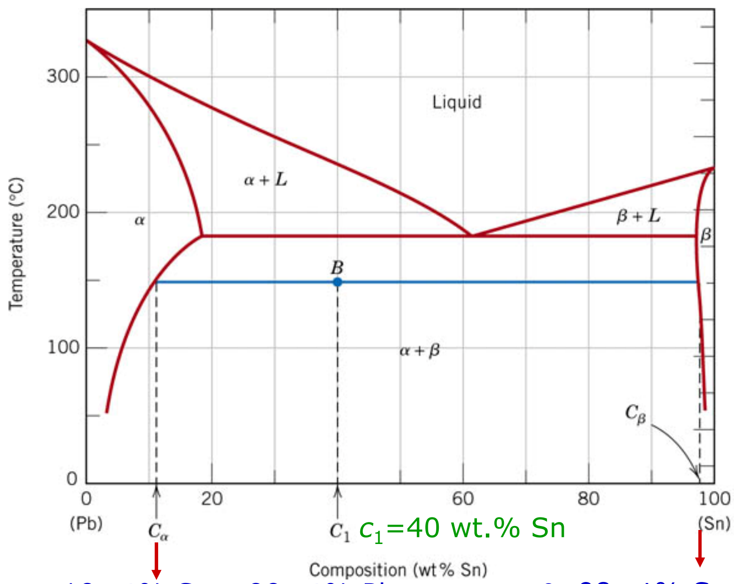
$$W_\alpha = \frac{c_\beta - c_0}{c_\beta - c_\alpha} = \frac{64}{95}$$
$$= 0.67 = 67\ \%$$

$$W_\beta = \frac{c_0 - c_\alpha}{c_\beta - c_\alpha} = \frac{31}{95}$$
$$= 0.33 = 33\ \%$$



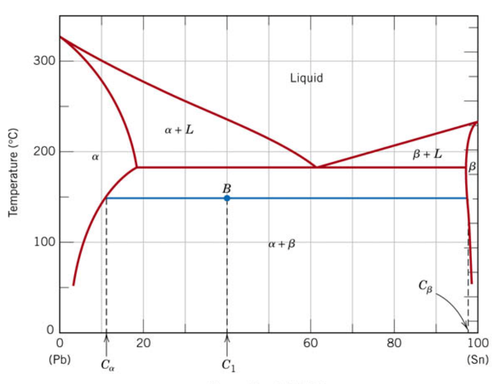
Binary eutectic system – composition

Example 40 wt.% Sn 60 wt.% Pb at 150 °C



Binary eutectic system – mass fraction

Example 40 wt.% Sn 60 wt.% Pb at 150 °C



$$W_\alpha = \frac{c_\beta - c_1}{c_\beta - c_\alpha} = \frac{98-40}{98-10} = 0.66 = 66\ \%$$

$$W_\beta = \frac{c_1 - c_\alpha}{c_\beta - c_\alpha} = \frac{40-10}{98-10} = 0.34 = 34\ \%$$

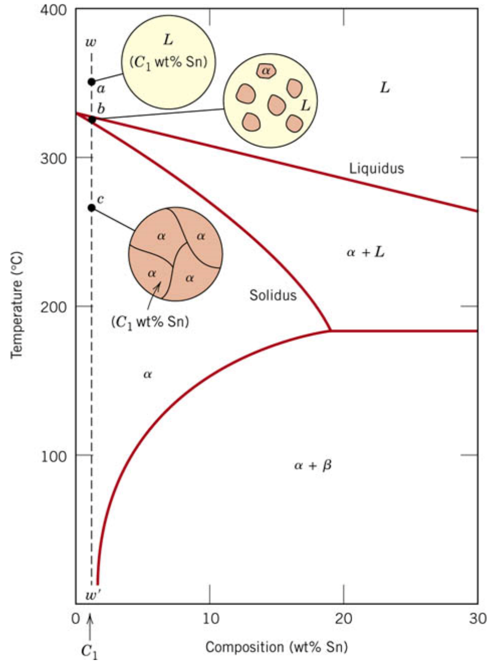
$$W = W_\alpha + W_\beta = 1 = 100\%$$

α phase and β phase

⇒ Lever rule

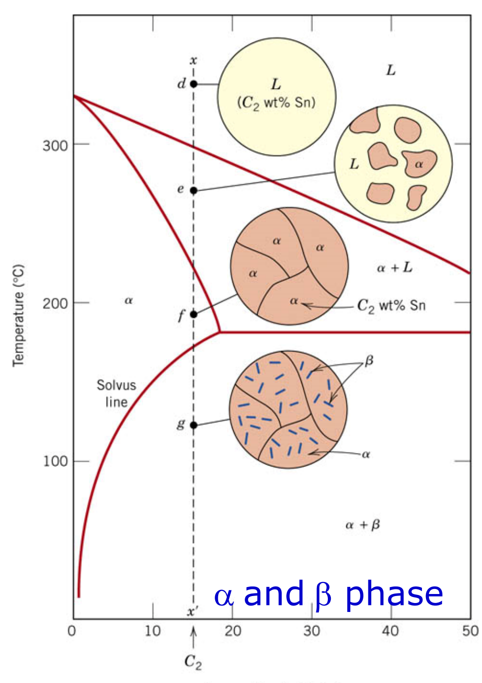
Microstructure – binary eutectic systems

- Entire content of B soluble in α at RT
- Single phase α or (A) as in isomorphous systems

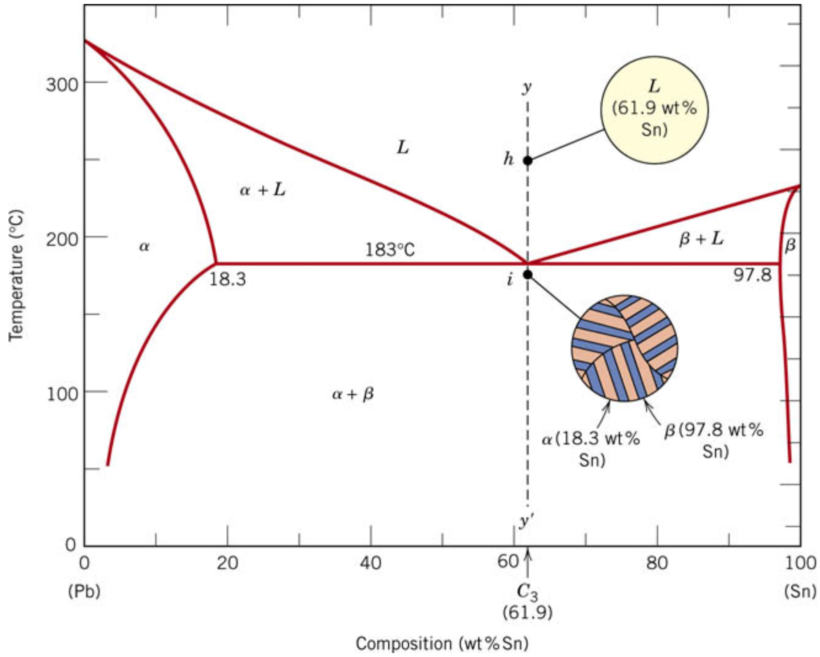


Microstructure – binary eutectic systems

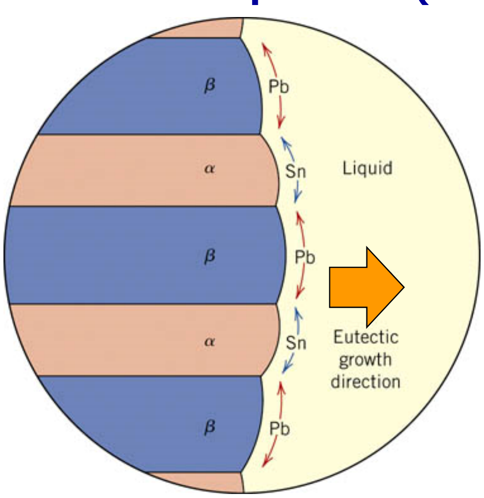
- Entire content of element B soluble in α at higher temperature, but not at RT
- Precipitates of β phase in α matrix at RT



Microstructure – binary eutectic systems
Eutectic composition (Pb-Sn)



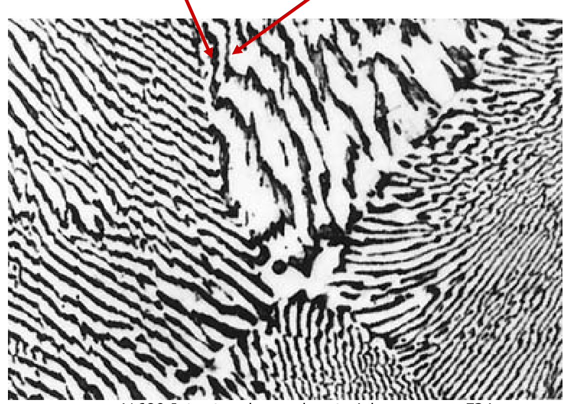
Microstructure – binary eutectic systems
Eutectic composition (Pb-Sn)



lamellar structure: alternating layers of α and β

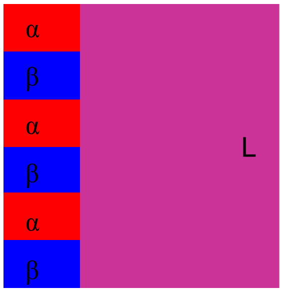
- Distance between lamellae depends on cooling rate
- Properties depend on distance between lamellae

Pb-rich α   Sn-rich β

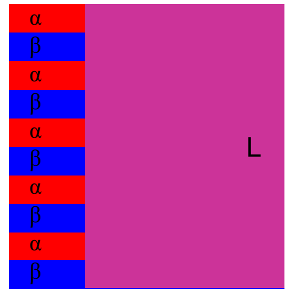


Eutectic solidification

- Slow solidification
- Wide lamellae



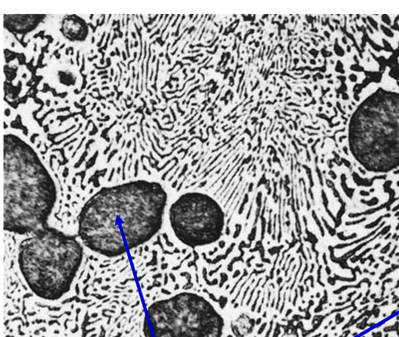
- Fast solidification
- Thin lamellae

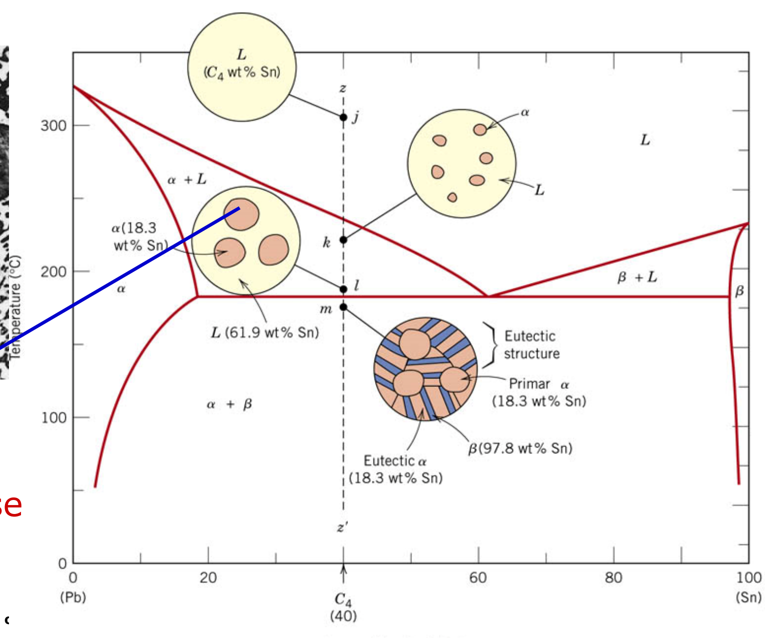


Mass fraction exactly same
in both cases (here 50%)

Microstructure – binary eutectic systems

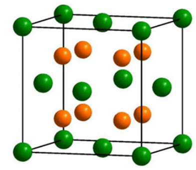
Hypo-eutectic composition (Pb-Sn)

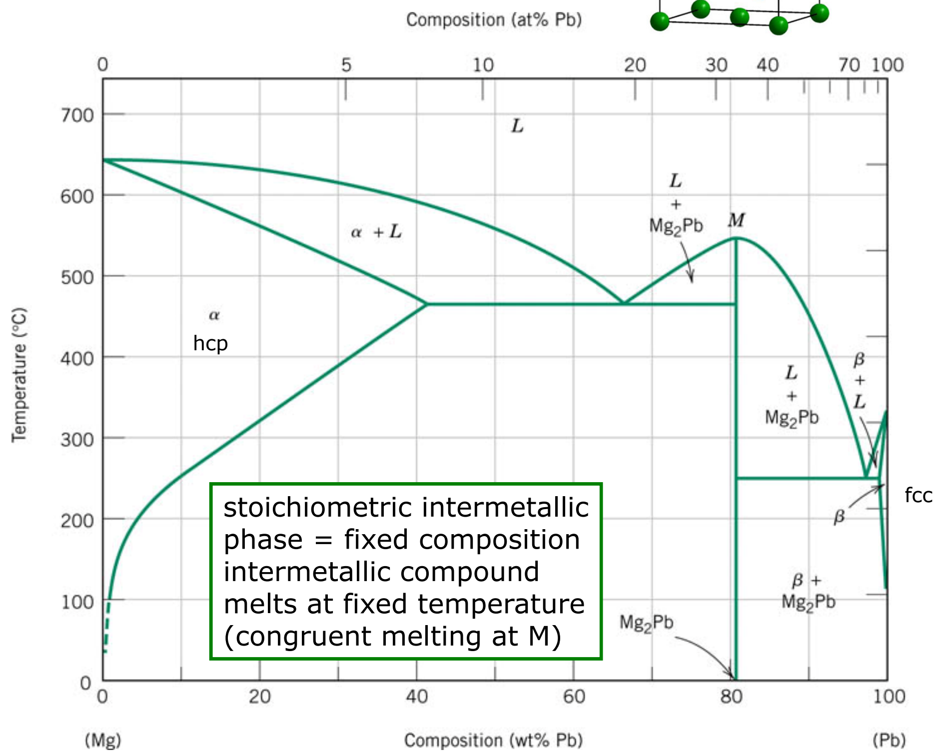




Primary phase:
pro-eutectic phase

Intermediate phases
Mg-Pb phase diagram





Demonstration of microstructure formation

Ansys
GRANTA EDUPACK

- Materials Science and Engineering – Database
  - Phase diagrams
  - Cooling paths
  - Pb-Sn (Eutectic)

Caveats

You must know how to read phase diagrams
(which information can be read form the diagram about the material and possible heat treatments)

but you do not have to learn the phase diagrams by heart
(they can be found in databases).

Exception: Complete solubility (isomorphous systems) or complete insolubility

Distinction between composition c and mass fraction W
c in wt.% (or at.%) W in %

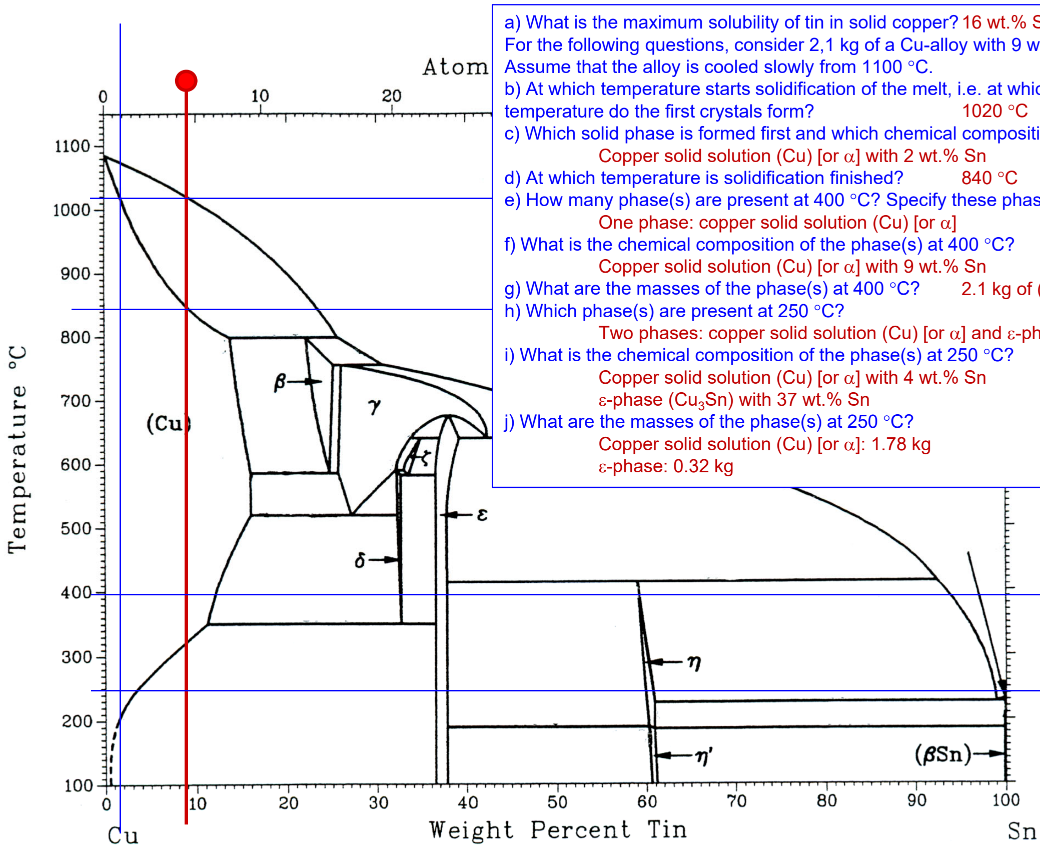
Composition vs. mass fraction
Two phase system: nut chocolate (100 g)

- Phase 1 chocolate
- Mass 75 g
- Mass fraction $W_1 = 75\%$
- Comp. $c_1 = 27$ wt.% fat

- Phase 2 hazel nuts
- Mass 25 g
- Mass fraction $W_2 = 25\%$
- Comp. $c_2 = 61$ wt.% fat

(Average) composition $c_0 = W_1 c_1 + W_2 c_2 = 35.5$ wt.% fat

Group exercises



a) What is the maximum solubility of tin in solid copper? 16 wt.% Sn

For the following questions, consider 2,1 kg of a Cu-alloy with 9 weight% Sn. Assume that the alloy is cooled slowly from 1100 °C.

b) At which temperature starts solidification of the melt, i.e. at which temperature do the first crystals form? 1020 °C

c) Which solid phase is formed first and which chemical composition has it?

Copper solid solution (Cu) [or α] with 2 wt.% Sn

d) At which temperature is solidification finished? 840 °C

e) How many phase(s) are present at 400 °C? Specify these phase(s).

One phase: copper solid solution (Cu) [or α]

f) What is the chemical composition of the phase(s) at 400 °C?

Copper solid solution (Cu) [or α] with 9 wt.% Sn

g) What are the masses of the phase(s) at 400 °C? 2.1 kg of (Cu) [or α]

h) Which phase(s) are present at 250 °C?

Two phases: copper solid solution (Cu) [or α] and ε-phase (Cu_3Sn)

i) What is the chemical composition of the phase(s) at 250 °C?

Copper solid solution (Cu) [or α] with 4 wt.% Sn

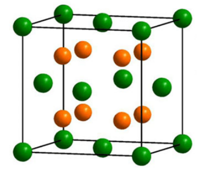
ε-phase (Cu_3Sn) with 37 wt.% Sn

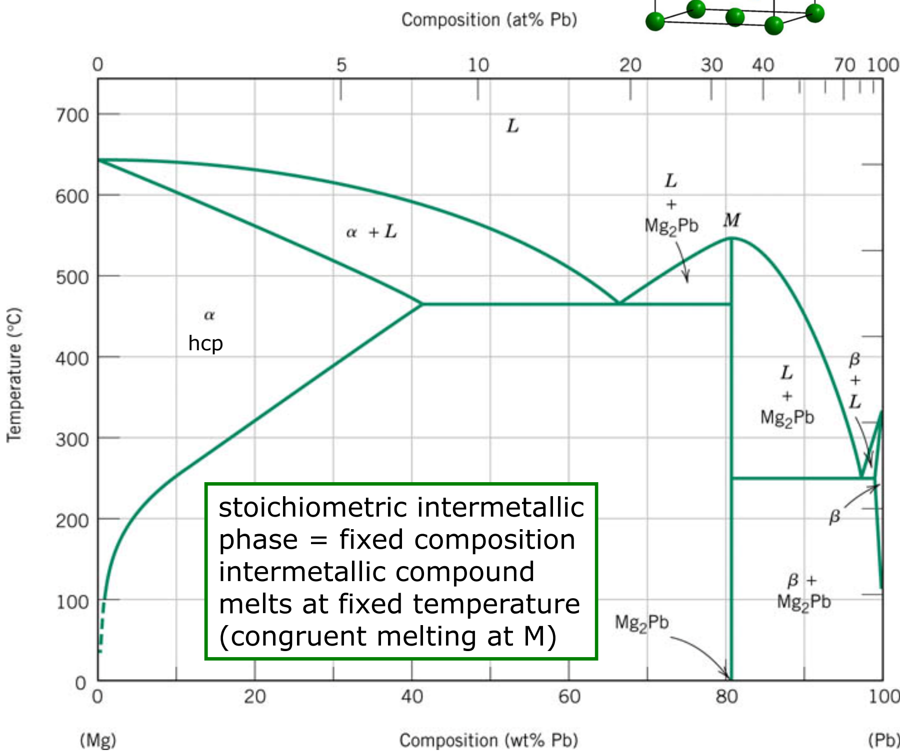
j) What are the masses of the phase(s) at 250 °C?

Copper solid solution (Cu) [or α]: 1.78 kg

ε-phase: 0.32 kg

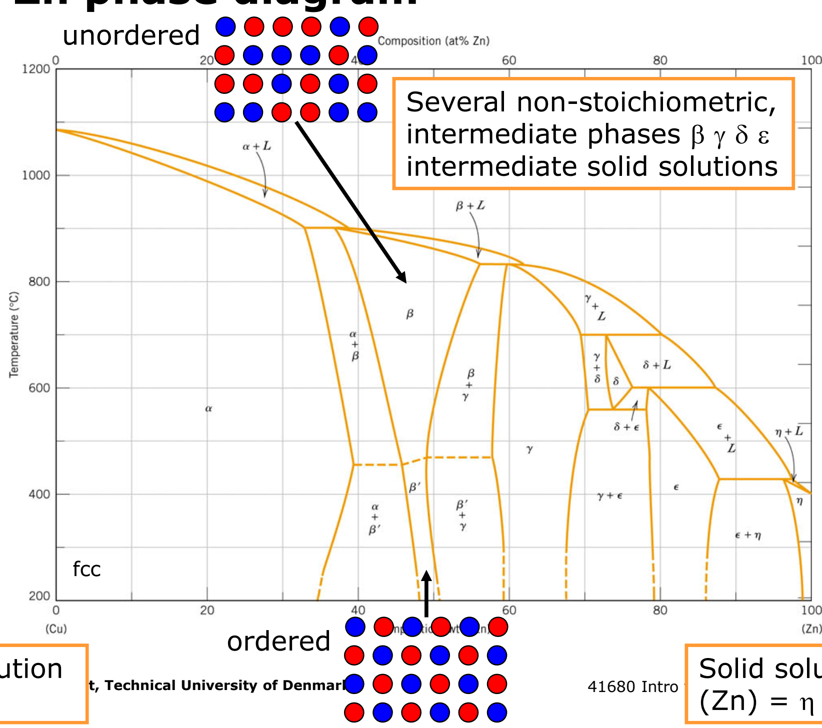
Intermediate phases
Mg-Pb phase diagram





stoichiometric intermetallic phase = fixed composition
intermetallic compound
melts at fixed temperature
(congruent melting at M)

Intermediate phases
Cu-Zn phase diagram

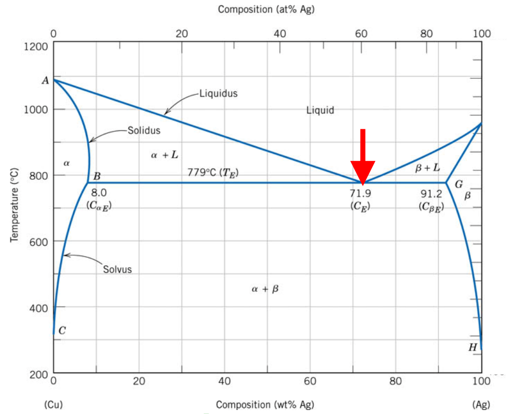


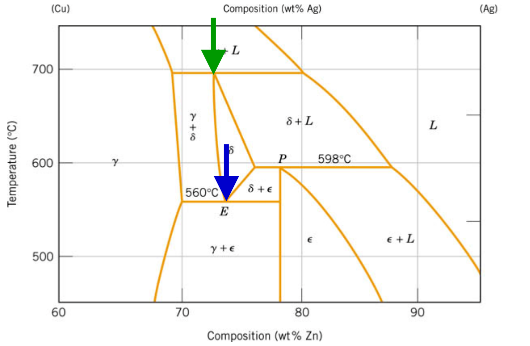
Several non-stoichiometric, intermediate phases β γ δ ε
intermediate solid solutions

Solid solution (Cu) = α

Solid solution (Zn) = η

Characteristic points: Eutectic, eutectoid, and peritectic transformations





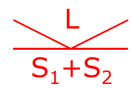
L = liquid

S = solid

S1, S2, S3 different solid phases

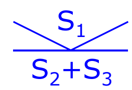
eutectic

$L \rightarrow S_1 + S_2$



eutectoid

$S_1 \rightarrow S_2 + S_3$



peritectic

$S_1 + L \rightarrow S_2$