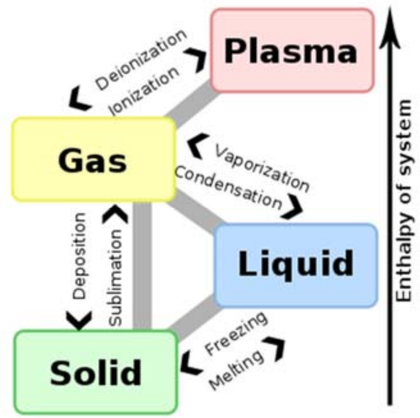
Physical bases of dental material science

phase transitions, properties of interfaces

Irén Bárdos-Nagy

General phase transitions

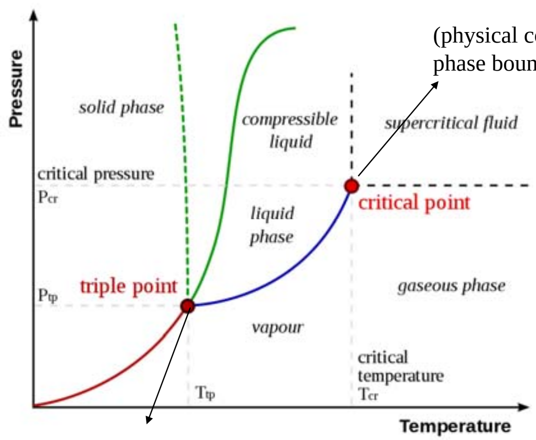
phase: physically and chemically homogeneuos part of the matereial



A typical phase diagram

phase diagram: graphical presentation of stable phases as a function of different parameters

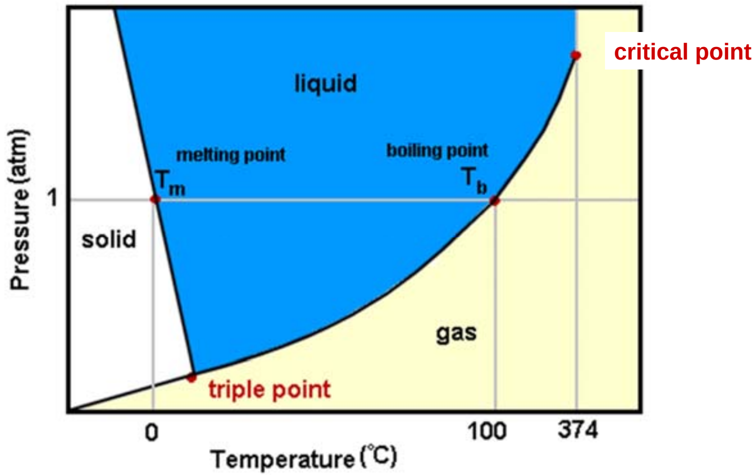
(physical conditions when the phase boundary ceases to exist)



(the three phases coexist in equlibrium)

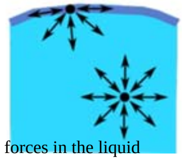
simultaneous transition of Ar from solid to liquid and to gas

Phase diagram of water



Properties of interfaces

Fluid-gas interfaces – *surface tension*



cohesive forces in the liquid

energy ΔE is required to increase the surface by an area ΔA

$$\sigma = \frac{\Delta E}{\Delta A} \quad \left(\frac{J}{m^2} = \frac{N}{m}\right)$$

surface tension

Surface tension of materials in air

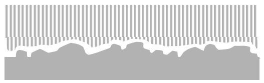
$$\sigma = \frac{\Delta E}{\Delta A} \quad \left(\frac{J}{m^2} = \frac{N}{m}\right)$$

material	σ (J/m^2)
liquid water	0,073
blood	0,06
saliva	0,05
paraffin	0,025
alcohol	0,023
dentine	0,092
enamel	0,087
Hg	0,484
PMMA	0,037

Liquid-solid interfaces - *Adhesion*

solid-solid contacts

solid-liquid



poor wetting

wetting

Liquid-solid interfaces - *Adhesion*

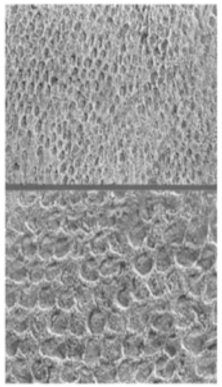
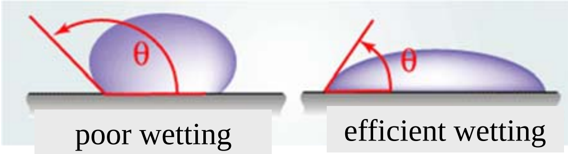


Figure 1. Morphological aspect of the surface of enamel conditioned with 36% phosphoric acid for 20 s. The formation of micropores with type I pattern of conditioning can be observed. (Original magnification: top, 750X; bottom, 1500X).

chemically purified surface of enamel

wetted surface of enamel

Conditions of wetting



θ : wetting angle

Young-equation:

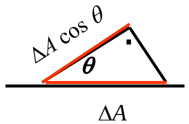
$\theta \uparrow \quad \cos\theta \downarrow$

if $\theta \leq 180^o$

$$\cos\theta = \frac{\sigma_{solid\text{-}air} - \sigma_{solid\text{-}liquid}}{\sigma_{liquid-air}}$$

Basic issue: what is energetically more favourable?

To form a solid-liquid or a solid-gas interface?



$$\Delta E = \Delta A \cdot \sigma_{s-l} - \Delta A \cdot \sigma_{s-air} + \Delta A \cos\theta \cdot \sigma_{l-air} = 0$$

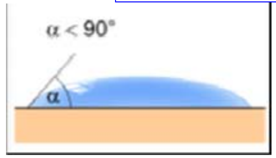
Young - equation

for the case of energy-minimum

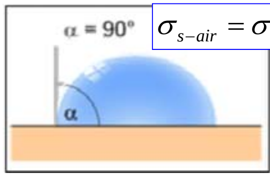
θ = α!!

Cases of wetting

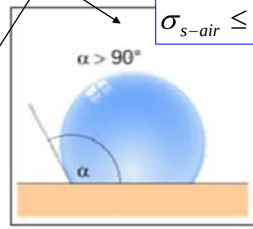
$\sigma_{s-air} \geq \sigma_{s-liquid}$

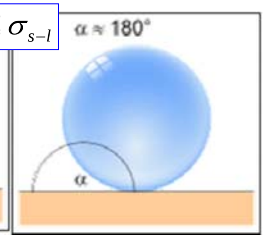


$\sigma_{s-air} = \sigma_{s-l}$



$\sigma_{s-air} \leq \sigma_{s-l}$





$$\cos\theta = \frac{\sigma_{solid\text{-}air} - \sigma_{solid\text{-}liquid}}{\sigma_{liquid-air}}$$

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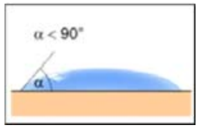
e.g.

liquid=water : 73 mJ/m^2
solid=glass: 130 mJ/m^2
glass-water: 60 mJ/m^2

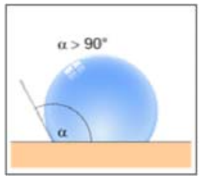
$\theta = 16{,}5$



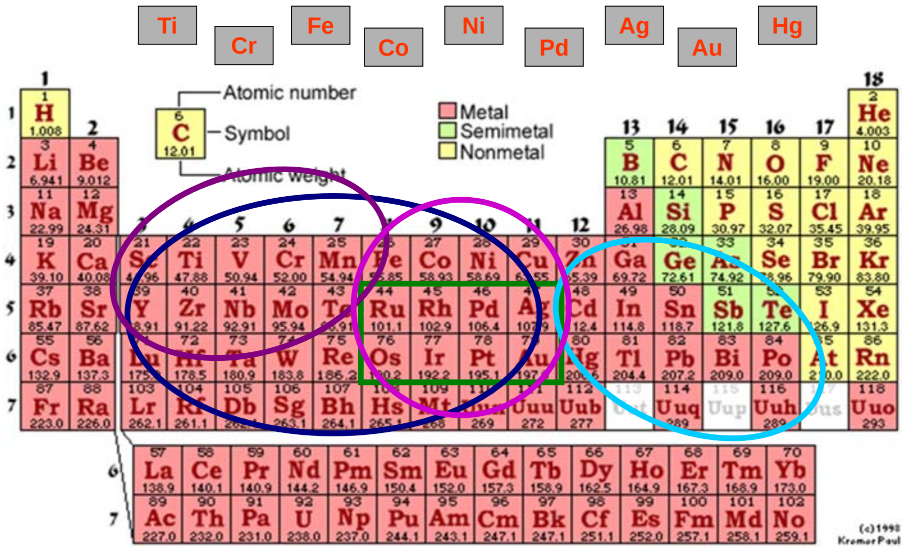
e.g.

liquid=Hg: 500 mJ/m^2
solid=glass: 130 mJ/m^2
glass–Hg: 430 mJ/m^2

$\theta = 127$



Crystallization, metals, alloyes
(metals applied in the dentistry)



high melting-point   precious metals   low melting-point

fragile   ductile


chromium


titanium


iron


nickel

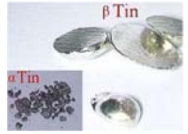

cobalt


palladium


silver


gold


mercury



tin

Properties of metals

-solid at room temperature (except Ga and Hg)

- high luster

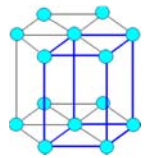
- relatively high density (tightly packed crystal lattice)

- large strength and toughness

- ability to be deformed under stress without cleaving (ductile)

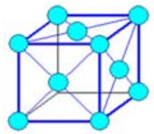
- good electric and thermal conductivity

Submicroscopic structure of metals


hexagonal

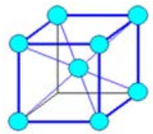
Ti, Cd, Co, Zn

Space filling factor 74 %


face-centered cubic

Ag, Au, Pd, Pt, Al, Cu, Ni

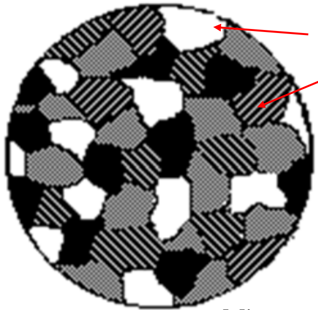
Space filling factor 74 %


body-centered cubic

Fe, Cr

Space filling factor 68 %

Microscopic structure of metals

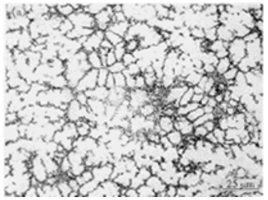


crystallites with different orientation, grains
small homogeneous particles

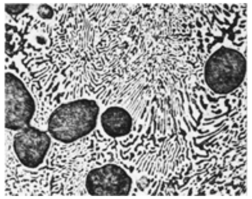
the properties of the material strongly depend on the structure

Stucture analysis: polishing (fine, rough)
chemical etching
microscopic technics

Microscopic view of metal surfaces



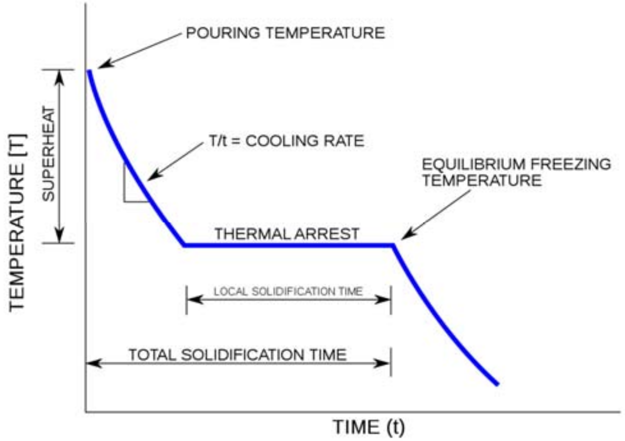
homogeneous



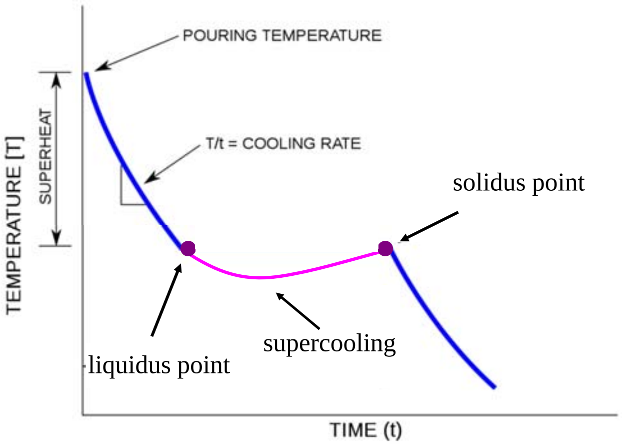
heterogeneous

Crystallization (phase transition from liquid to solid phase)

cooling curve



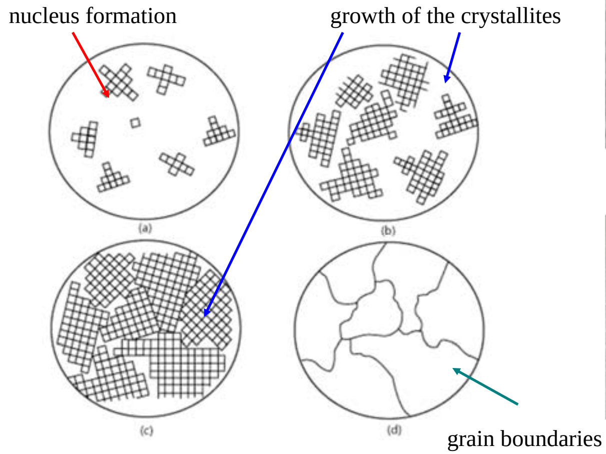
Supercooling (phase transition from liquid to solid phase)



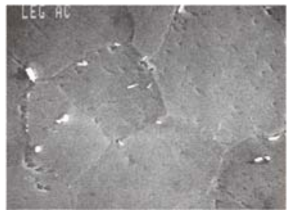
Transition from the liquid to the solid state

two stages: a./ nucleus (seed crystal) formation

b./ crystal growth



dentritic (tree) increase



isotrope increase

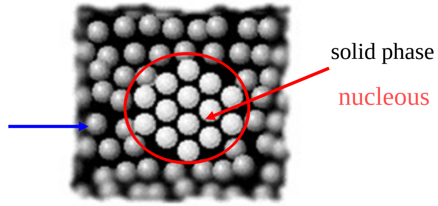
The role of the size and the shape of the grains !!

manganese dentrites on a limestone

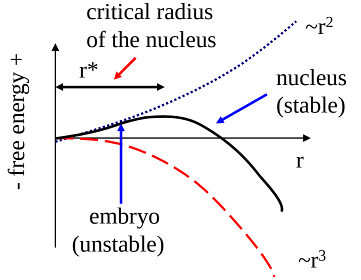
snow crystal

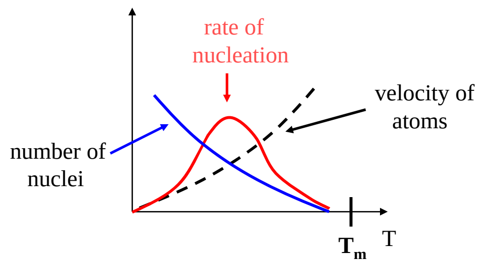
Nucleus formation

a./ homogeneous nucleation



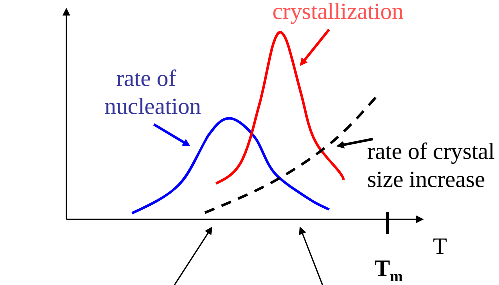
important parameters: the size of the nucleus
the rate of nuleus formation





b./ heterogeneous nucleation (on the wall of the dish, impurities, dislocations mainly earlier and faster crystallization)

Effect of the rate of crystal growth



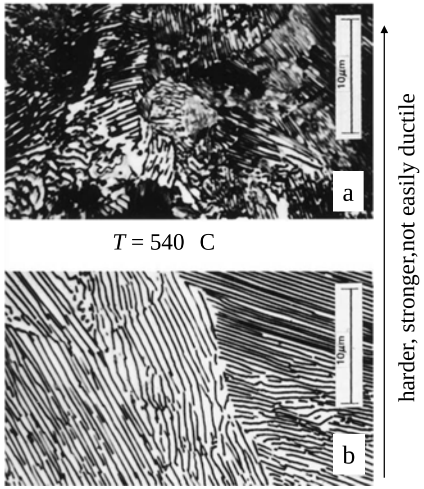
fast nucleation and low rate of crystal increase

low rate of nucleation and fast increase of crystal size

result

fine grain structure (a)

rough grain structure (b)

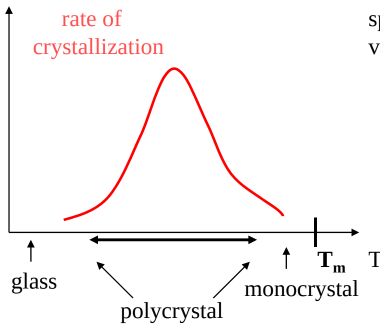


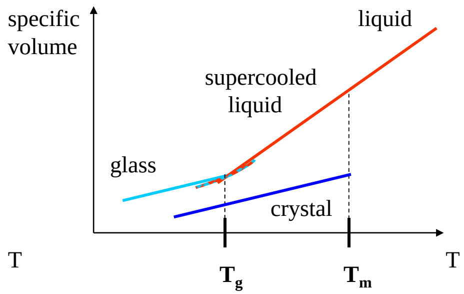
T = 540 C

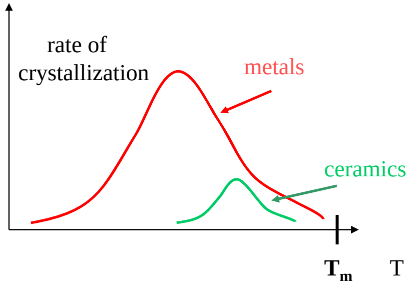
T = 690 C (T_o = 727 C)

solid – solid state conversions !!

Crystallization ⟷ glass formation





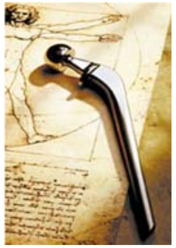


Alloyes

partial or comlete solid solutions of one or more elements in a metallic matrix

metal + metal (Fe+Cr+Ni, Au+Cu)

metal + non metal (Fe+C)



The aim: to modify (to improve) the properties

- hardness and rigidity (Au + Cu)
- tensile strength
- shear strength
- to avoide or reduce the corrosion (Fe, Co, Ni, + Cr)
- to increase the adhesion on metal-ceramic surfaces (precious metal+Fe, Sn, In)

Determination of composition

weight % : $$c_1 = \frac{m_1}{m_1 + m_2} \cdot 100(\%)$$

properties!!

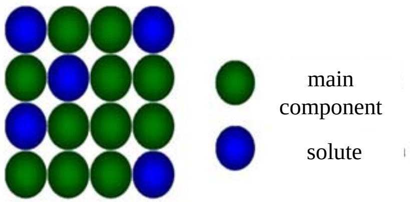
molar % : $$x_1 = \frac{\nu_1}{\nu_1 + \nu_2} \cdot 100(\%)$$

Classification:

- according the application (inlay, corona of teeth)
- on the base of the main component (Au, Pd, Pt, Fe)
- on the base of the number of components (biner, terner, quaterner)
- on the base of the main 3 components (Au-Pd-Ag, Ni-Cr-Be)
- on the base of the phase diagram (solid solution, eutectic alloy, peritectic alloy, metal compound)

Solid solutions

substitutional



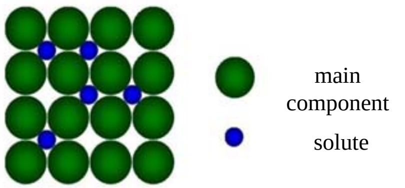
examples: Cu-Ni, Pd-Ag, Au-Cu, ...

homogeneous structure

criteries of formation

similar atomic radii (less then 15% diff.)
same crystal structure
similar electronegativities
similar valency

interstitial



examples: Fe-C, CP Ti (O, C, N, H), ...

the atomic radius of the solute is smaller
the amount of the solute is less than 10%

properties of solid solutions

flexibility changes

strength increases

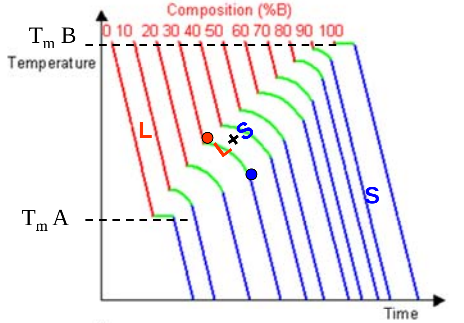
hardness increases

ductility changes

plasticity decreases

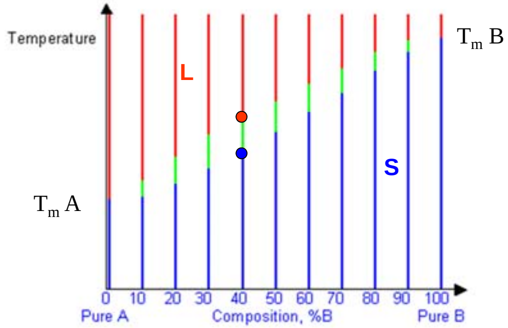
metal	**atomic radius (nm)**	**lattice**	**electro-negativity**
Au	0,2882	fcc	2,4
Pt	0,2775	fcc	2,2
Pd	0,2750	fcc	2,2
Ag	0,2888	fcc	1,9
Cu	0,2556	fcc	1,9
Ni	0,25	fcc	1,8
Sn	0,3016	tetragonal	1,8

cooling curve of solid solutions

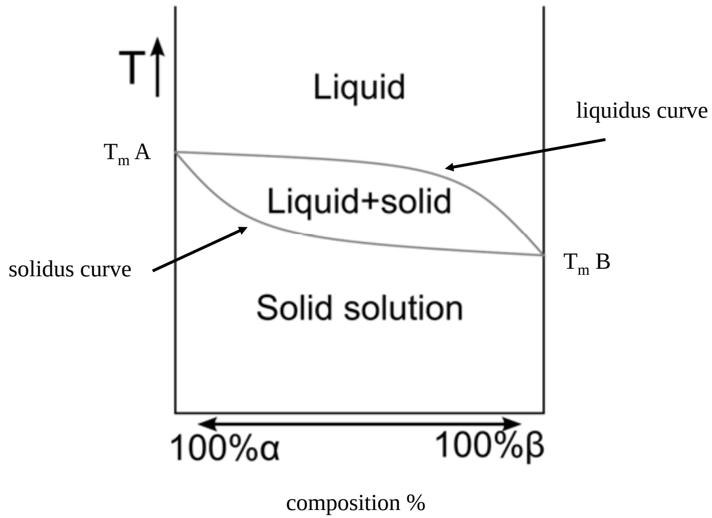


phase diagram of solid solutions

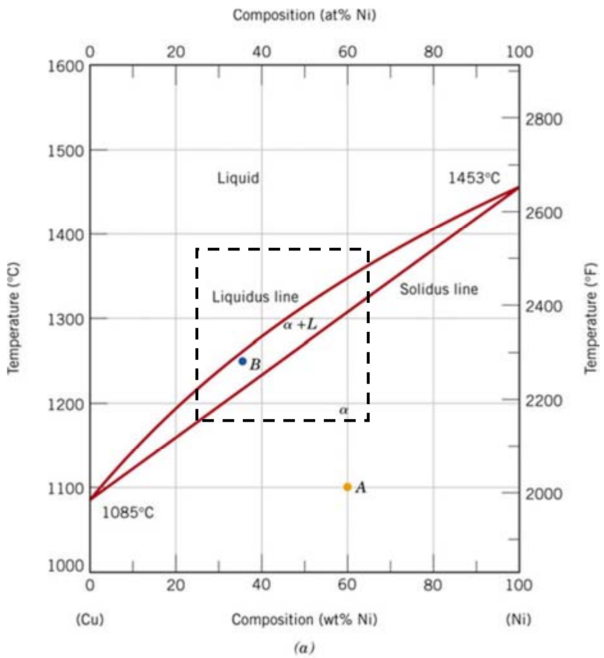
equilibrium !!



equilibrium

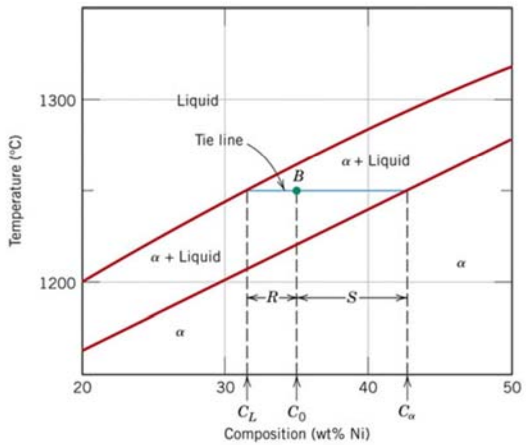


example:
Cu + Ni



Calculation of the composition and the ratio of the different phases

what is the composition at the B point



Liquid phase composition:

31,5 wt % Ni + 68,5 wt % Cu

Solid phase composition:

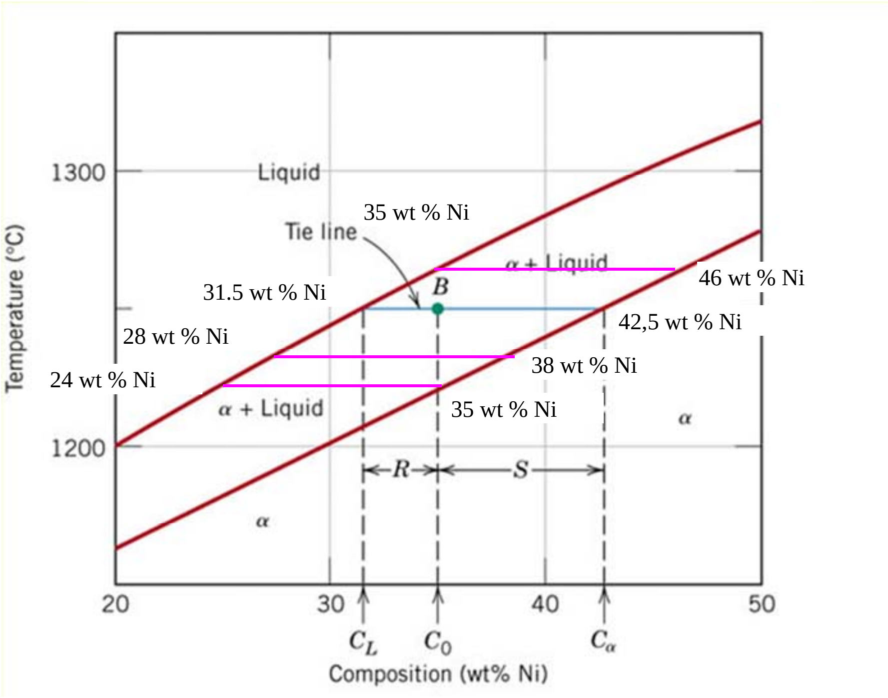
42,5 wt % Ni + 57,5 wt % Cu

Liquid phase ratio:

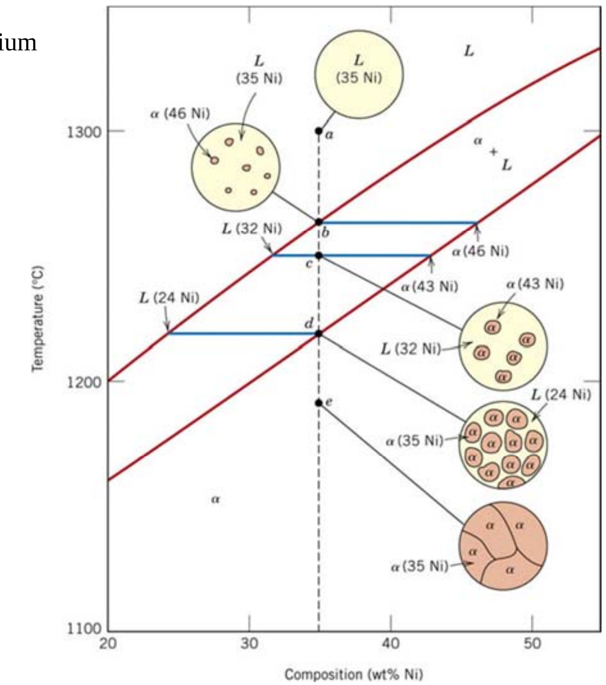
$$\frac{S}{R+S} = 68\%$$

Solid phase ratio:

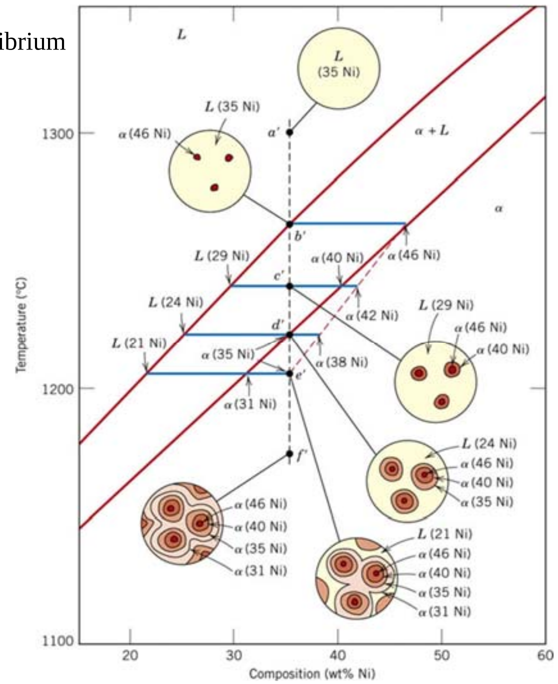
$$\frac{R}{R+S} = 32\%$$



equilibrium



non equilibrium cooling



segregation

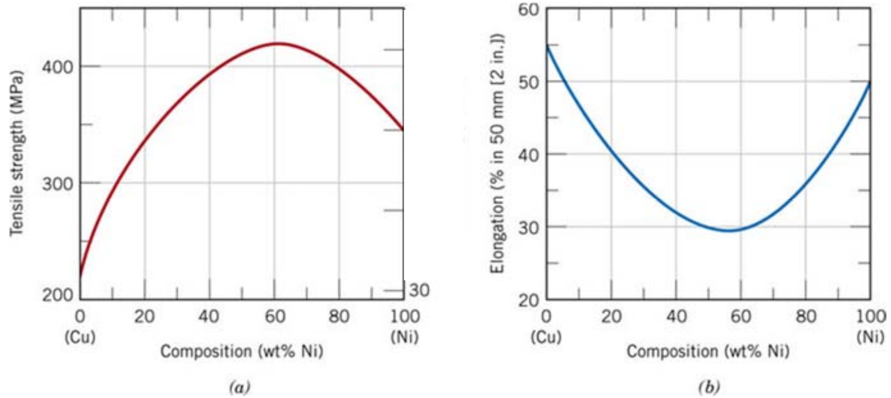
seedy structure

heterogeneous

↓

homogenization

Influence of the solute material on different physical properties of alloyes



Metal compounds

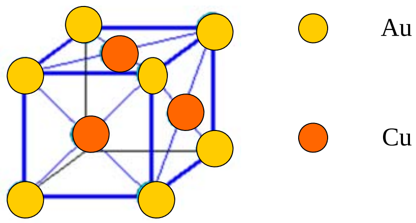
Definite stochiometry

example: Au-Cu

50 wt %Au-50 wt %Cu

< 400 C

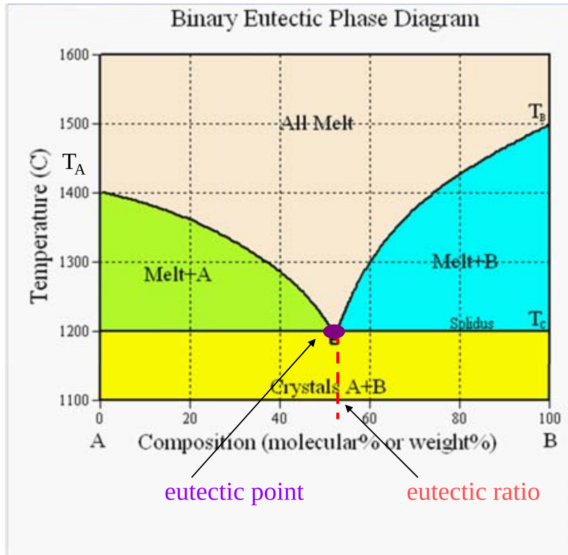
$AuCu_3$



in the amalgam: Ag_3Sn

Cu_6Sn_5

Eutectic alloys



insolubility in the solid phase

↓

pure metal crystallites

↓

heterogenious structure

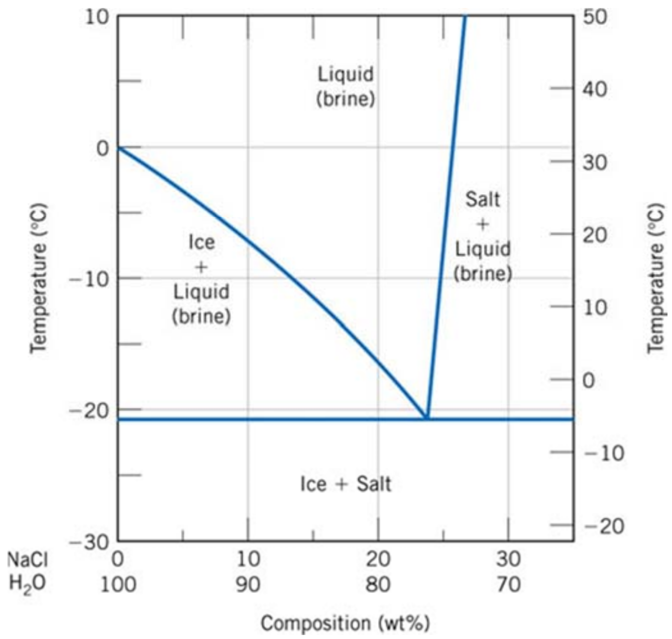
examples

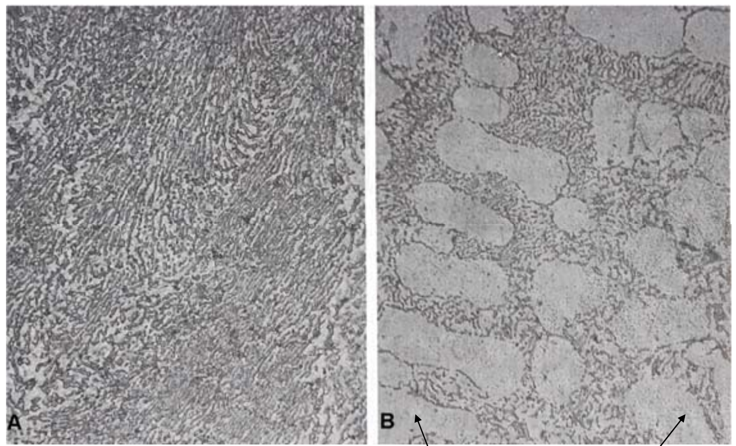
77% H_2O+23 % NaCl

T_E = – 21 C

Wood-metal (Bi-Pb-Cd-Sn)

T_E = 68°C



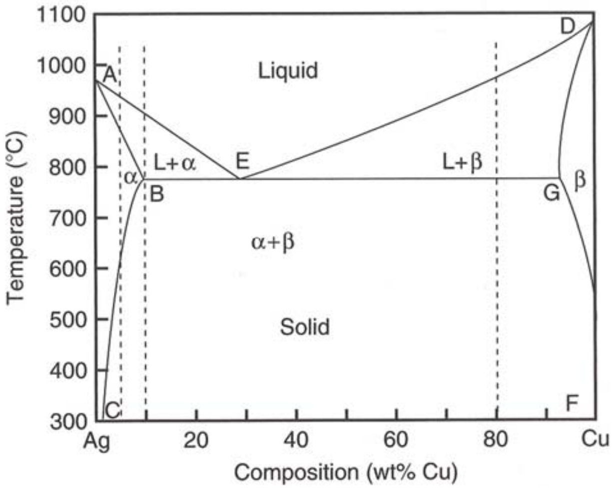


62%Sn-38%Pb

eutectic alloy

75%Sn-25%Pb

(Sn rich islands)

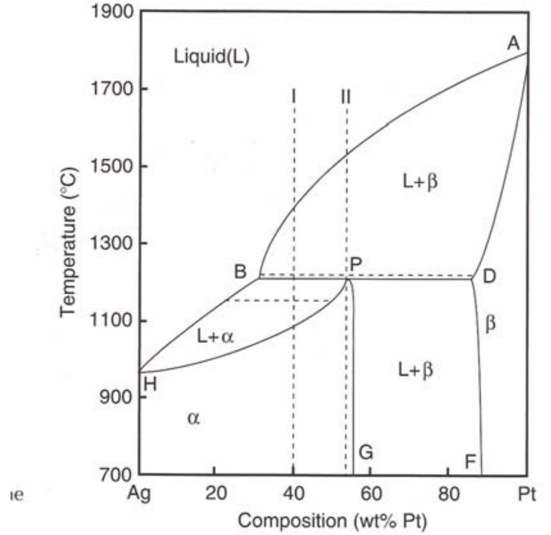


Peritectic alloys

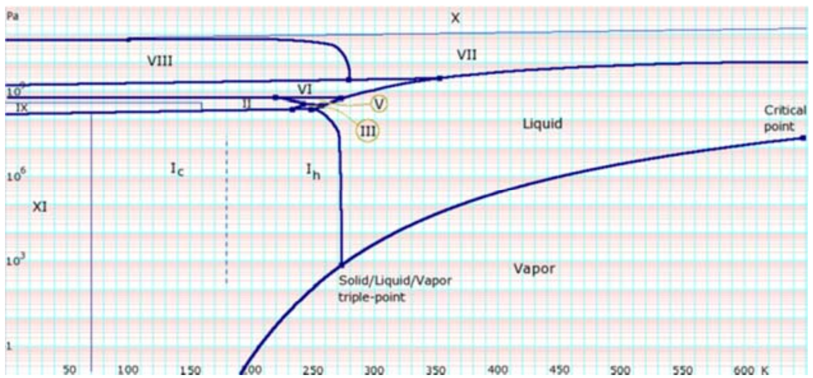
examples:

Ag-Sn

Ag-Pt



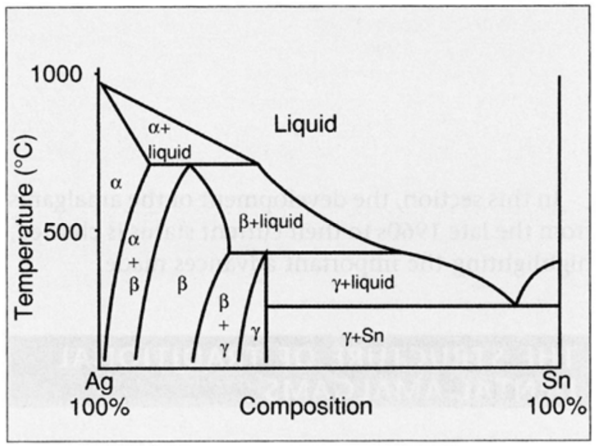
Phase diagram of polymorphic and polyamorphic systems



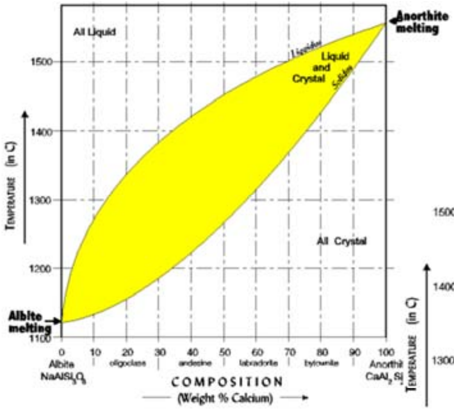
Phase diagram of water

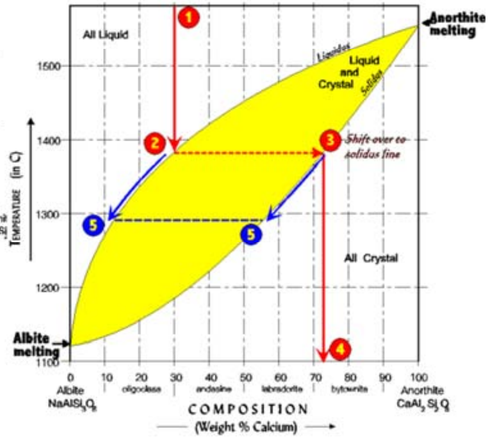
dental amalgam

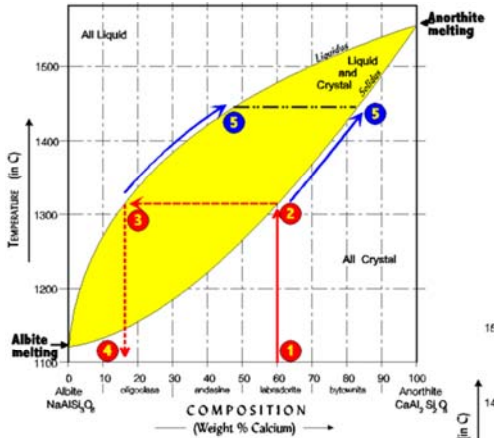
composition	
metal	**% (wt/wt)**
Hg	50
Ag	34
Sn	13
Cu	2
Zn	1

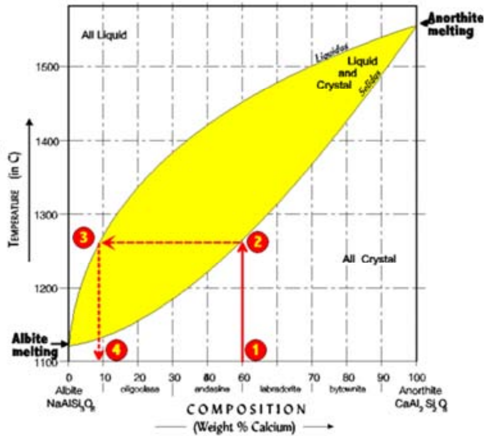


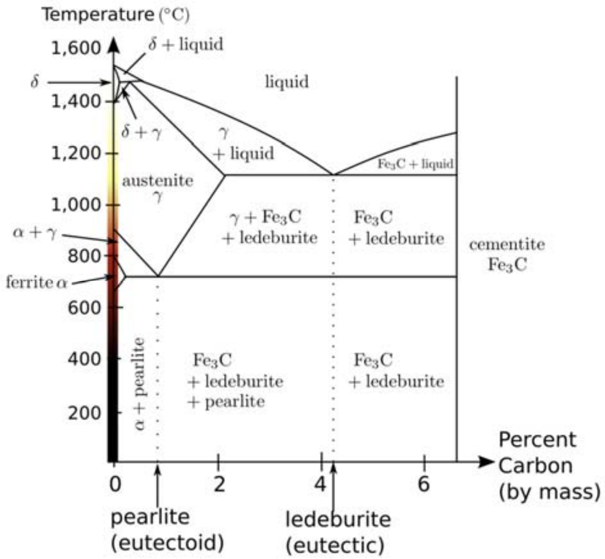
γ phase: Ag_3Sn


All Liquid
Liquid and Crystal
Liquidus
Solidus
All Crystal
Anorthite melting
Albite melting
TEMPERATURE (in C)
1500
1400
1300
1200
1100
0 10 20 30 40 50 60 70 80 90 100
Albite NaAlSi3O8
oligoclase
andesine
labradorite
bytownite
Anorthite CaAl2Si2O8
COMPOSITION
(Weight % Calcium)


All Liquid
Liquid and Crystal
Liquidus
Solidus
All Crystal
Anorthite melting
Albite melting
Shift over to solidus line
1
2
3
4
5
5
TEMPERATURE (in C)
1500
1400
1300
1200
1100
0 10 20 30 40 50 60 70 80 90 100
Albite NaAlSi3O8
oligoclase
andesine
labradorite
bytownite
Anorthite CaAl2Si2O8
COMPOSITION
(Weight % Calcium)


All Liquid
Liquid and Crystal
Liquidus
Solidus
All Crystal
Anorthite melting
Albite melting
1
2
3
4
5
5
TEMPERATURE (in C)
1500
1400
1300
1200
1100
0 10 20 30 40 50 60 70 80 90 100
Albite NaAlSi3O8
oligoclase
andesine
labradorite
bytownite
Anorthite CaAl2Si2O8
COMPOSITION
(Weight % Calcium)


All Liquid
Liquid and Crystal
Liquidus
Solidus
All Crystal
Anorthite melting
Albite melting
1
2
3
4
TEMPERATURE (in C)
1500
1400
1300
1200
1100
0 10 20 30 40 50 60 70 80 90 100
Albite NaAlSi3O8
oligoclase
andesine
labradorite
bytownite
Anorthite CaAl2Si2O8
COMPOSITION
(Weight % Calcium)


Temperature (°C)
1,600
1,400
1,200
1,000
800
600
400
200
δ + liquid
δ
δ + γ
liquid
γ + liquid
Fe3C + liquid
austenite γ
γ + Fe3C + ledeburite
Fe3C + ledeburite
cementite Fe3C
α + γ
ferrite α
α + pearlite
Fe3C + ledeburite + pearlite
Fe3C + ledeburite
0
2
4
6
Percent Carbon (by mass)
pearlite (eutectoid)
ledeburite (eutectic)