Department of Civil Engineering
IIT Madras

Development of Microstructure

Modern Construction Materials - Lecture 5
Prof. Ravindra Gettu
IIT Madras

Microstructure

The details of the structure of a solid can usually be seen only at high magnifications under a microscope; therefore, such details are called the *microstructure*.

Microstructure

Formation of Different Kinds of Microstructures

Conditions	Material	Remarks
Crystallization from melts	Metal Igneous rocks	
Precipitation or crystallization from solution	Hardened cement paste; Clays	Amorphous and crystalline components
Solidification without crystallization	Silicate glass Thermoplastics	Limited crystallization for some plastics
Solidification from gas phase	Silica fume Carbon black	Amorphous powders
Sintering of inorganic powders	Ceramics Bricks	May involve reaction between two kinds of powders, and/or partial melting (liquid phase sintering)

Young et al.

Microstructure

- Metals, polymers and glasses are generally formed by solidification from melts.
- Solidification does not always involve crystallization. Unlike metals, the solid structure of polymers and inorganic glasses is amorphous (i.e., non-crystalline).

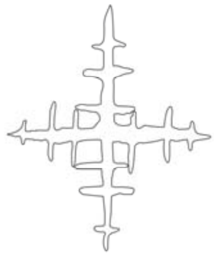
Microstructure

- Most substances, including metals, can form a glassy structure if the cooling rates are fast enough. On the other hand, some polymers can crystallize partially if the cooling rates are slow enough.
- Cementitious materials develop microstructures by solidification from solutions. The solutions are made up of a reactive solid and a liquid. The products can be mainly amorphous (e.g., portland cement) or crystalline (e.g., calcium aluminate cement).

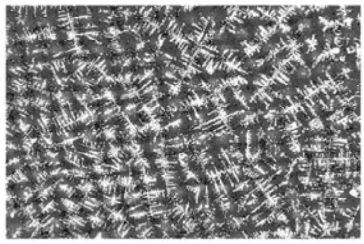
Young et al.

Crystallisation from Melts

- The tendency for crystal growth to occur along preferential directions can lead to a branched or *dendritic* structure.
- The growth stops when the dendrites meet. The points of contact build irregular polygonal surfaces(e.g., *grain boundaries*).
- The solid acquires a granular appearance.



Dendritic structure of an antimony-lead alloy



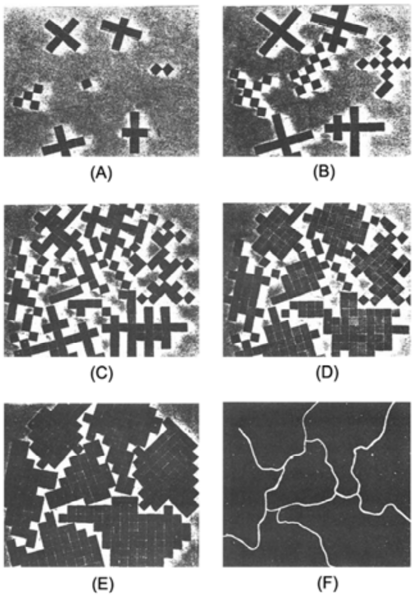
Crystal growth in preferred directions – dendrite (schematic)

Rosenthal

Crystallisation from Melts

The growth can be represented as:

- the formation of nuclei (A),
- the growth the dendritic crystals (B & C),
- the meeting of the dendrites growing from different nuclei and further crystallisation (D), and
- the formation of grain boundaries to result in a polycrystalline solid (E & F).



Schematic interpretation of crystal growth

Rosenthal

Crystallisation from Melts

- At the temperature of melting (T_m), there is as much chance for a nucleus to be absorbed by the melt as to be precipitated. So, at this temperature, the rate of nucleation is nil.
- The rate of nucleation increases as the temperature is decreased further, and is maximum when the melt is undercooled (or supercooled) to a critical temperature (T_{cr}).
- Impurities act as artificial centres of nucleation, called *seeds*. The presence of seeds can stimulate crystallisation above the critical temperature (T_{cr}).

Rosenthal

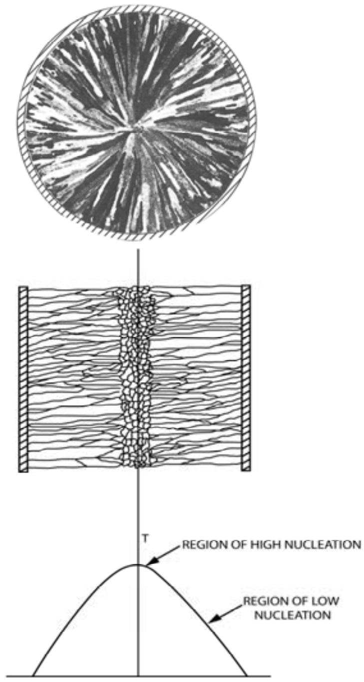
Crystallisation from Melts

- The crystals are *equiaxed* when the temperature of the melt is uniform.
- When the temperature is non-uniform (i.e., there is a temperature gradient), different sizes and shapes of crystals occur.

Rosenthal

Crystallisation from Melts

- When a molten metal is poured into a mould from which heat is extracted, the temperature drops radially.
- The temperature of crystallisation is reached first at the sides leading to small equiaxed crystals covering the wall.
- Then, small crystals grow inwards as columnar grains.
- At the centre, the temperature gradient is low and equiaxed grains occur.



Rosenthal

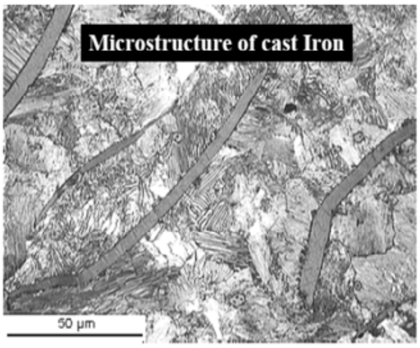
Crystallisation from Solution

- Crystallisation can also occur from solutions. Here, nucleation and growth are governed by the degree of *supersaturation*.
- Saturation occurs when the crystal is in equilibrium with its solution, so the rate of dissolution is equal to the rate of crystallization.
- Temperature plays an important role by changing the level of saturation.
- Once crystals have formed, their rate of growth depends on the diffusion of ions to the growing faces.

Young et al.

Phases

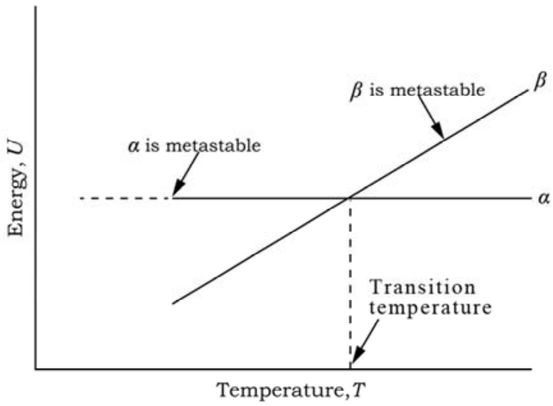
A *phase* is a homogenous region in a system on which the properties are uniform. It has a specific composition and atomic structure. It can consist of one component or multiple components.



This is an alloy of Fe with 4 wt.% C. There are several phases. The long gray regions are flakes of graphite. The matrix is a fine mixture of BCC Fe and Fe_3C compound.

Phase Changes on Heating and Cooling

Energy diagram for two phases α and β (two different packing of atoms in a crystal, or two different states of matter).



- Phase α has lower energy at higher temperatures and is the stable phase while β is stable at lower temperatures. At the transition temperature, the two energies are equal.

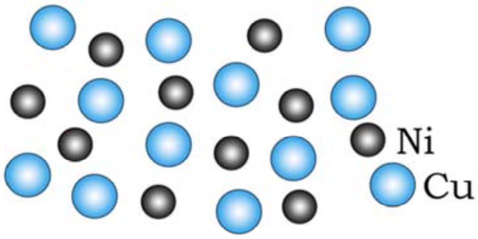
Phase Changes on Heating and Cooling

- The metastable phases will exist only if there is some energy barrier for the nucleation of the stable phase.
- The metastable phase may be induced to change to the stable phase at a later time by the application of additional energy (mechanical or thermal) or by the addition of seed crystals.

Young et al.

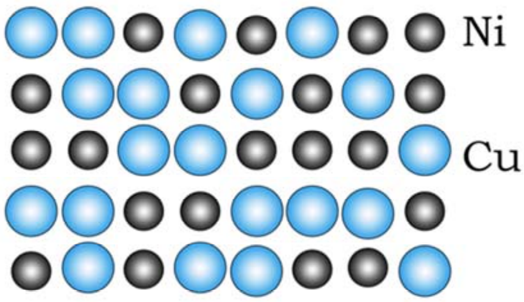
Solid Solutions

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



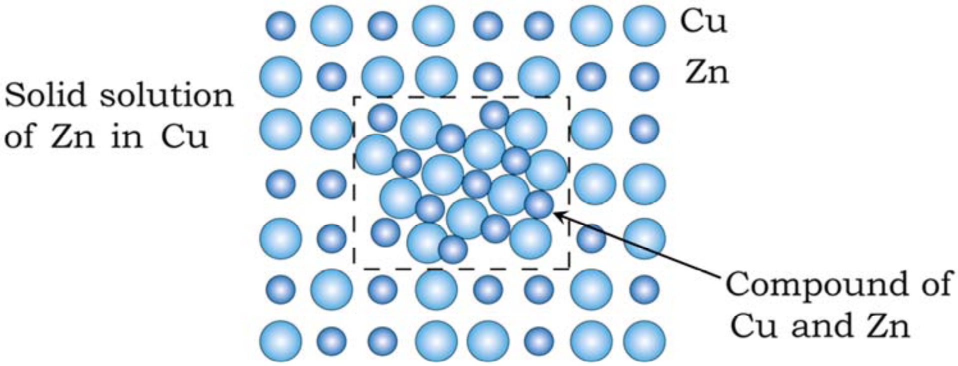
Solid Solutions

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



Solid Solutions

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



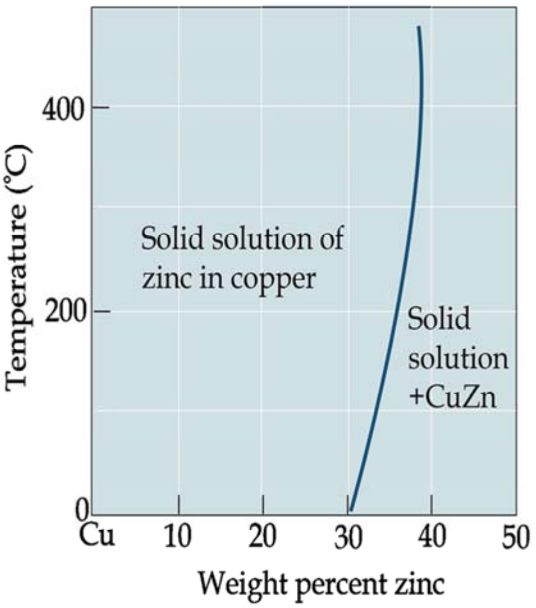
Solid Solutions

Solubility limit is the maximum concentration of solute atoms that may dissolve in the solvent to form a solid solution.

Solid Solutions

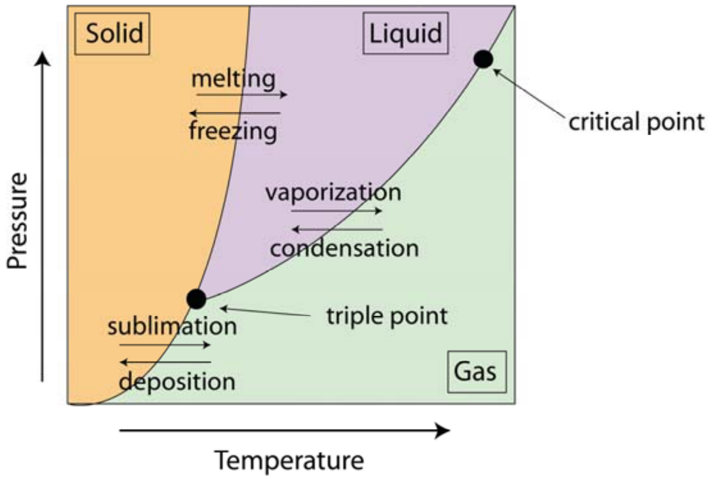
The solubility of zinc in copper

The solid line represents the solubility limit; when excess zinc is added, the solubility limit is exceeded and two phases coexist.



Phase Diagrams

A *phase diagram* is a graphical representation of the combinations of temperature, pressure, composition or other variables for which the specific phases exist at equilibrium.



Phase Diagrams

Gibb's Phase Rule

If the number of degrees of freedom are represented by f, the number of phases (that coexist) by p and the number of components in the system by n, then

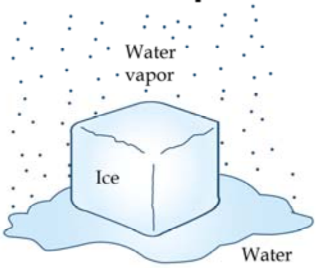
$$f + p = n + 2$$

At constant atmospheric pressure, $f + p = n + 1$

For example, in a two component single phase molten alloy at constant pressure, $f = 2$; i.e., within certain limits, both temperature and composition can be varied independently.

Phase Diagrams

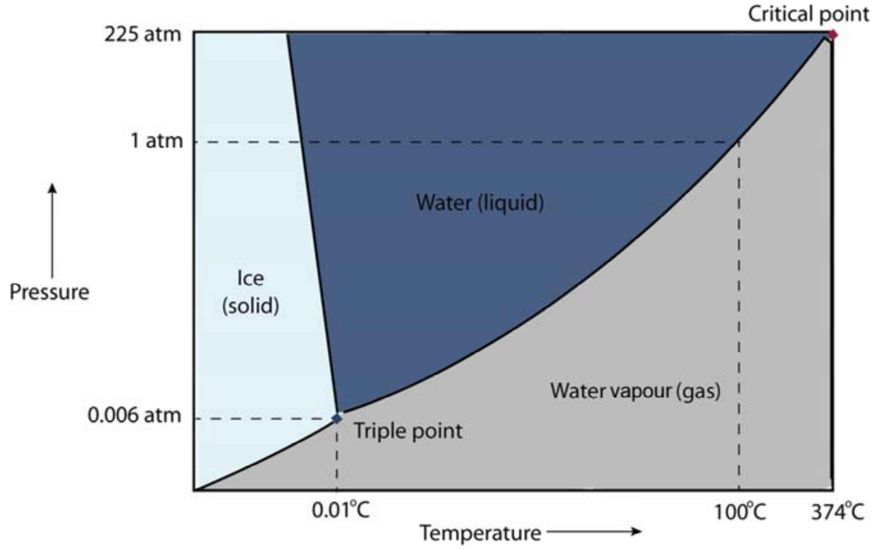
Single component system: Ice-Water-Vapour



- $n = 1$ (H_2O); $f + p = 3$.
- For one phase, $f = 2$; i.e., both temperature and pressure can vary.
- For two phases to co-exist, $f = 1$; i.e., only temperature or pressure can vary independently.
- For three phases to co-exist, $f = 0$.

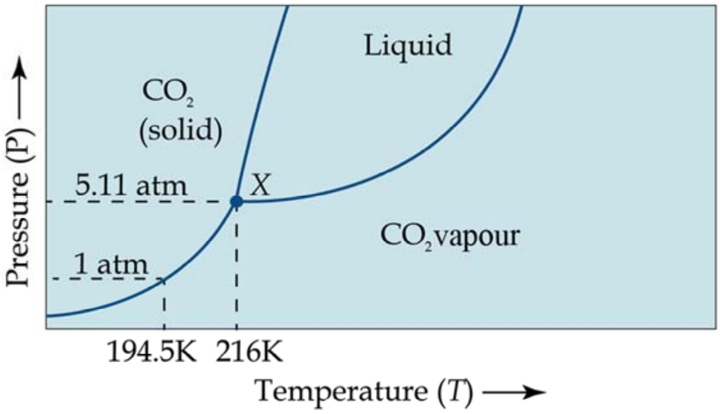
Phase Diagrams

Single component system: Ice-Water-Vapour



Phase Diagrams

Single component system: Carbon dioxide



At normal pressure (1 atm), CO_2 solid (dry ice) passes directly to CO_2 gas, as the temperature increases.

Single component system: Iron

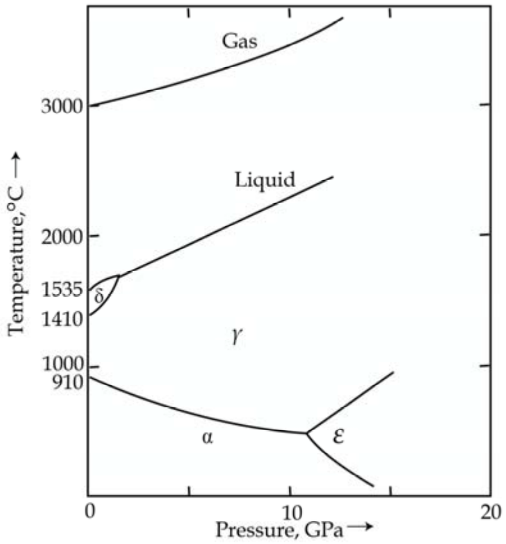
Phase Diagrams

The equilibrium crystal form of iron at normal temperature is BCC (α).

On heating to 910°, α changes over to FCC (γ).

On further heating to 1410°, γ changes over to BCC (δ) form.

When very high pressure is applied (15 GPa), BCC iron transforms to HCP (ε) phase.



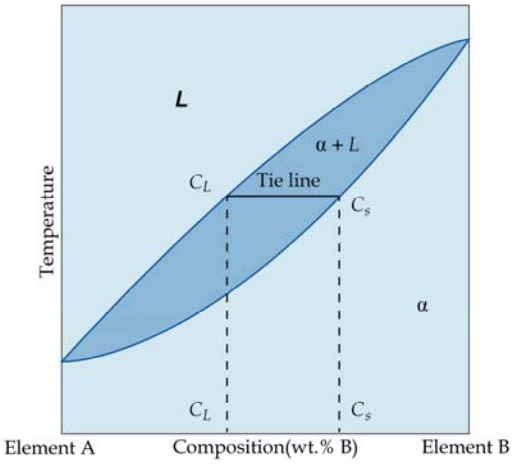
Raghavan

Binary Phase Diagrams

- Binary phase diagrams are drawn for two component systems at atmospheric pressure with temperature and composition as the variables (i.e., $f + p = n + 1$).
- In binary phase diagrams, a two-phase region always separates a single phase region – the "1-2-1" rule.

Binary Phase Diagrams

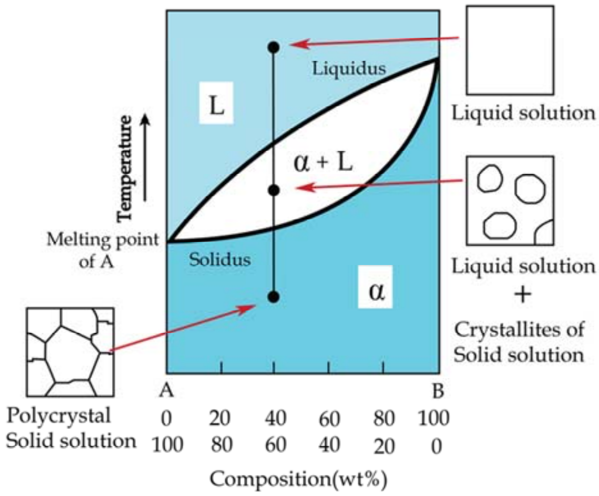
Hypothetical phase diagram between elements A & B exhibiting complete liquid solubility and solid solubility. The two components dissolve in each other in all proportions both in the liquid and solid state; $f + p = 3$



In the two phase region, a tie line fixes the composition for every temperature ($f = 1$); i.e., C_L gives the composition of the liquid and C_S gives the composition of the solid.

Binary Phase Diagrams

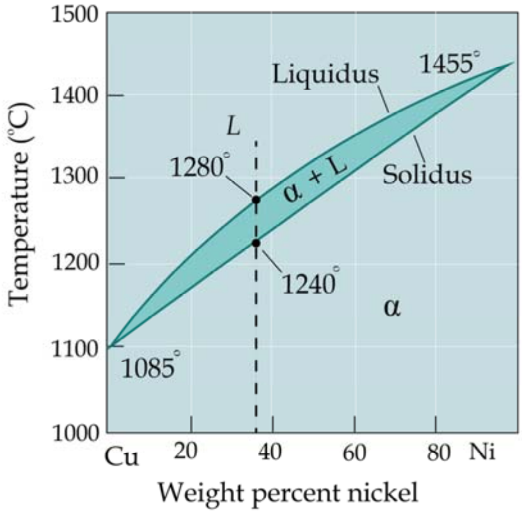
In multi-component systems, melting occurs over a range of temperatures, between the solidus and liquidus lines. Solid and liquid phases are in equilibrium in this temperature range.



Binary Phase Diagrams

Cu-Ni Alloy

(Complete solubility occurs since both Cu and Ni have the same FCC crystal structure, atomic radius and valency.)



Binary Phase Diagrams

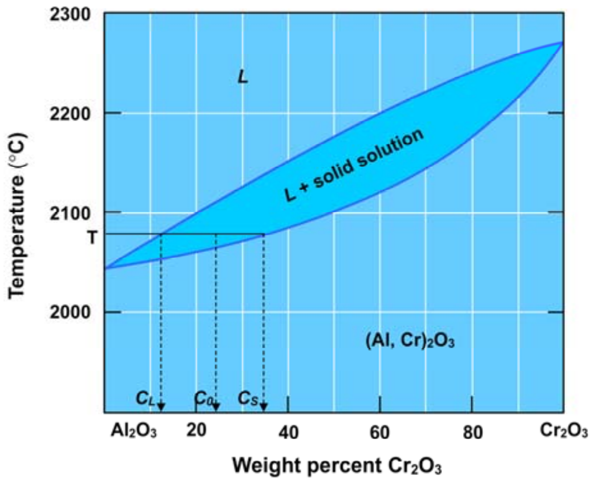
Liquidus temperature - The temperature at which the first solid begins to form during solidification.

Solidus temperature - The temperature below which all liquid has completely solidified.

<u>Melting temperature of alloy depends on the composition.</u>

Binary Phase Diagrams

Al_2O_3-Cr_2O_3 phase diagram

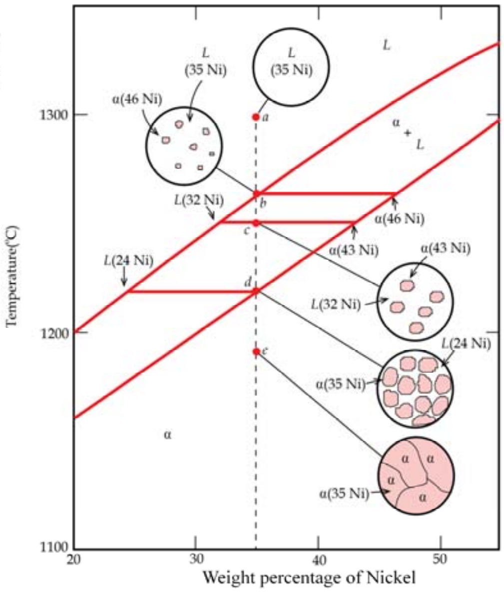


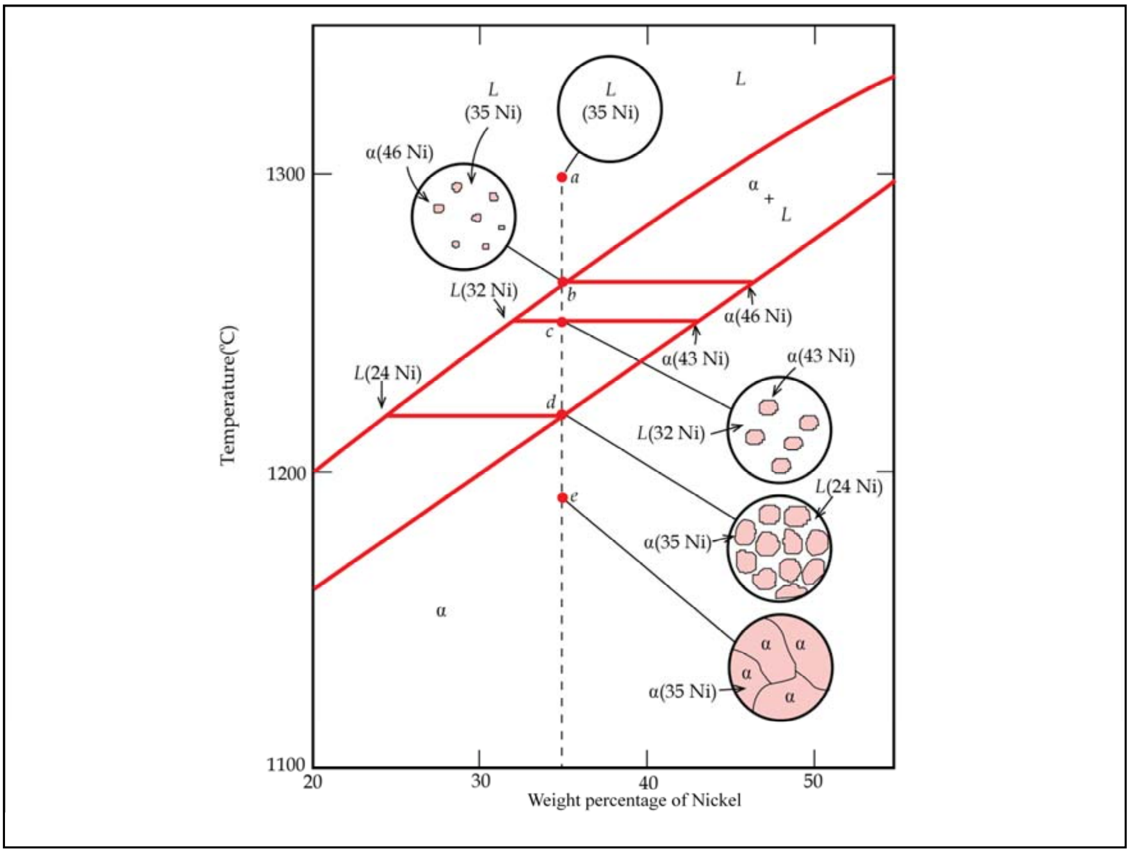
- At temperature *T*, for an overall composition of c_0% of Cr_2O_3 :
- the liquid composition is c_L% of Cr_2O_3
- the solid composition is c_S% of Cr_2O_3
- the % liquid: $100\,(c_S - c_0)\,/\,(c_S - c_L)$

Binary Phase Diagrams

Development of the microstructure under very slow cooling

Cu-Ni Alloy phase diagram




L
(35 Ni)
L
(35 Ni)
L
α(46 Ni)
1300
a
α
+
L
L(32 Ni)
b
α(46 Ni)
c
α(43 Ni)
α(43 Ni)
L(24 Ni)
d
L(32 Ni)
Temperature(°C)
1200
e
L(24 Ni)
α(35 Ni)
α
α
α
α
α
α(35 Ni)
1100
20
30
40
50
Weight percentage of Nickel

Binary Phase Diagrams

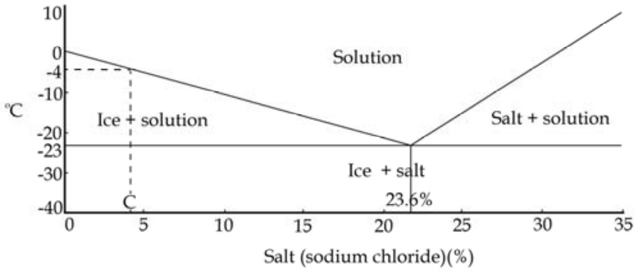
Alloy with 35% Ni and 65% Cu

- Solidification in the solid+liquid phase occurs gradually upon cooling from the liquidus line.
- The compositions of the solid and the liquid change gradually during cooling.
- Nuclei of the solid phase form and they grow to consume all the liquid at the solidus line.

Binary Phase Diagrams

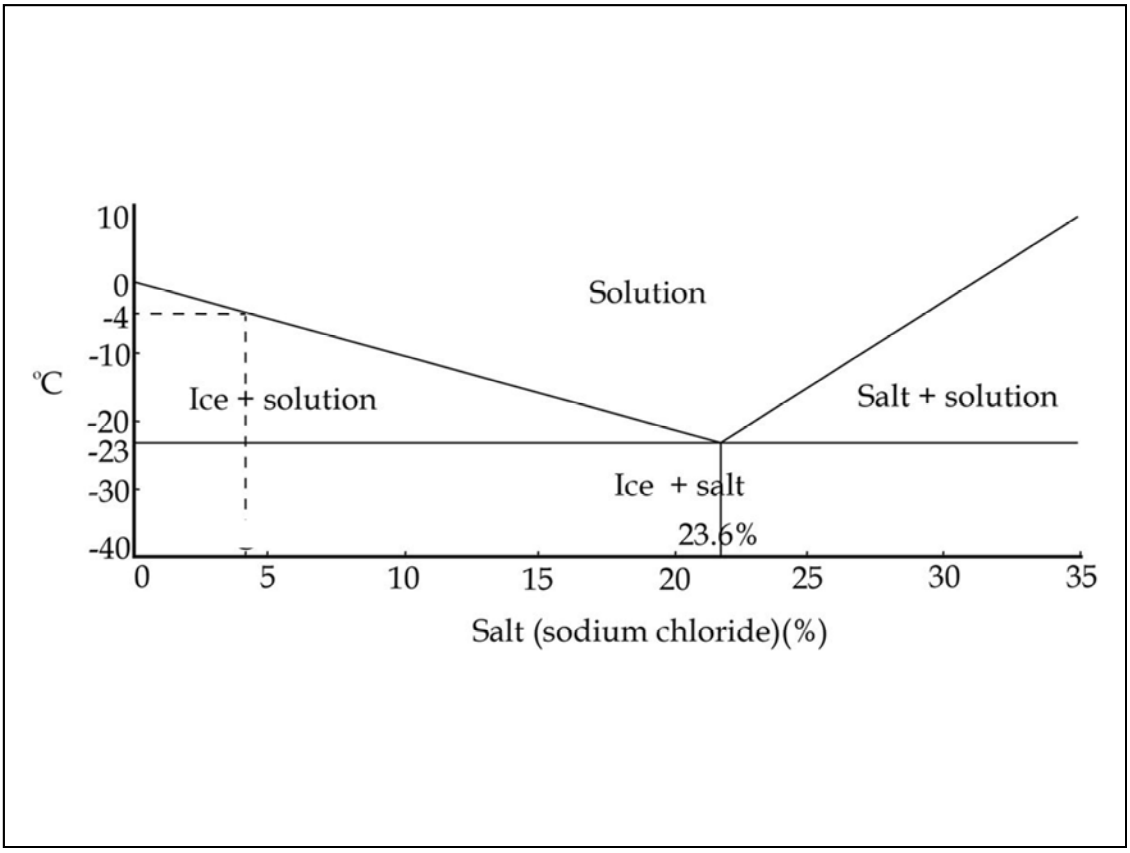
Substances that are completely soluble as liquids but totally insoluble as solids

Ice-Salt (NaCl)



- Ice and solution are in equilibrium between -4 and -23°C. So when a small amount of salt is mixed with ice, in this range, the ice begins to melt and a "slush" is formed.
- *Explains why salt is used on icy roads*

Higgins


10
0
-4
-10
°C
-20
-23
-30
-40
Solution
Ice + solution
Salt + solution
Ice + salt
23.6%
0
5
10
15
20
25
30
35
Salt (sodium chloride)(%)

Binary Phase Diagrams

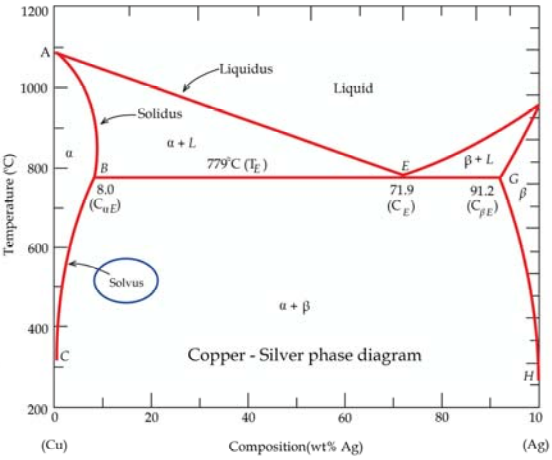
Three single phase regions (α – solid solution of Ag in Cu, β – solid solution of Cu in Ag, & Liquid)

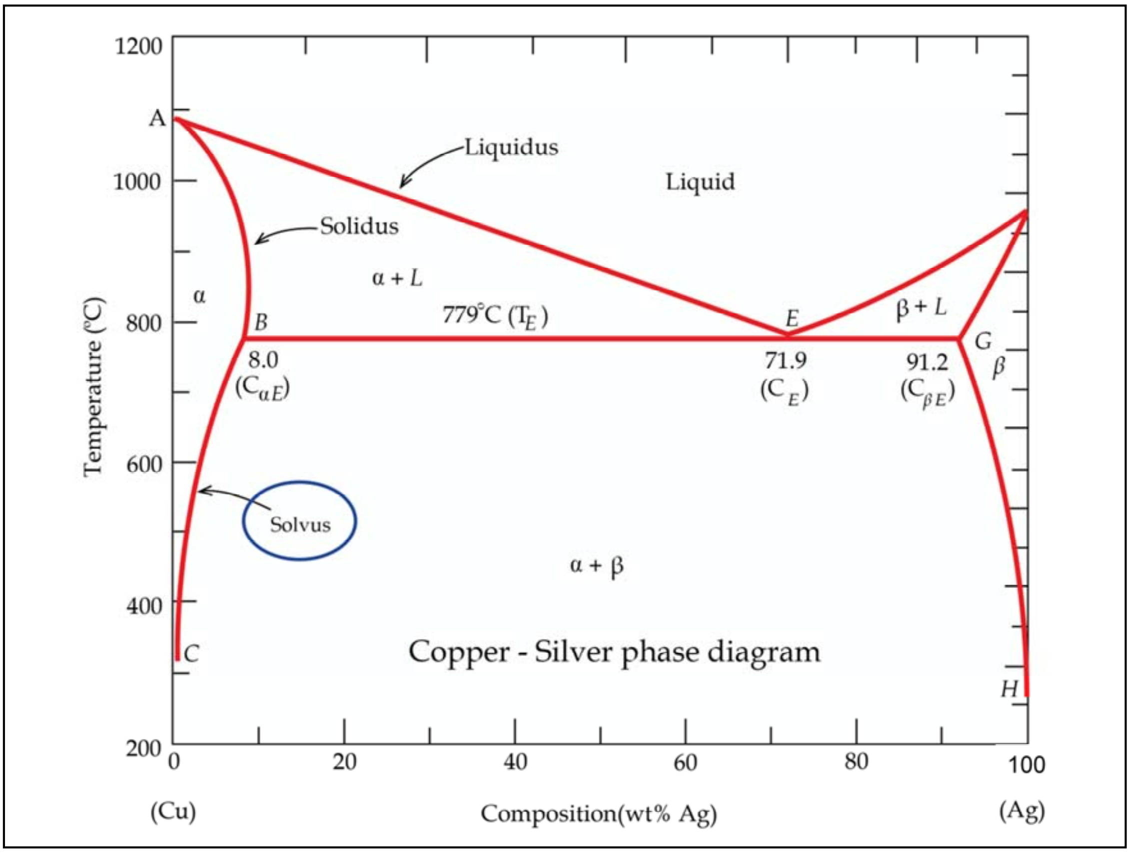
Three two-phase regions (α+L, α+β, β+L)

Solvus line separates one solid solution from a mixture of solid solutions. It gives the limit of solubility.

Alloys with limited solubility (Eutectic systems)

<u>Copper-Silver</u>




1200
A
1000
800
600
400
200
Temperature (°C)
Liquidus
Liquid
Solidus
α + L
α
B
779°C (T_E)
E
β + L
G
β
8.0
($C_{\alpha E}$)
71.9
(C_E)
91.2
($C_{\beta E}$)
Solvus
α + β
C
Copper - Silver phase diagram
H
0
20
40
60
80
100
(Cu)
Composition(wt% Ag)
(Ag)

Binary Phase Diagrams

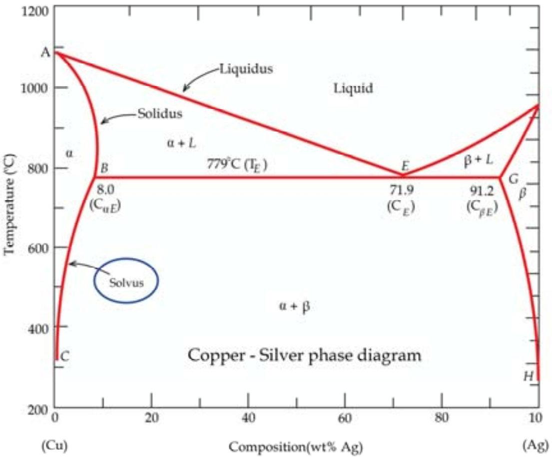
Three single phase regions (α – solid solution of Ag in Cu, β – solid solution of Cu in Ag, & Liquid)

Three two-phase regions (α+L, α+β, β+L)

Solvus line separates one solid solution from a mixture of solid solutions. It gives the limit of solubility.

Alloys with limited solubility (Eutectic systems)

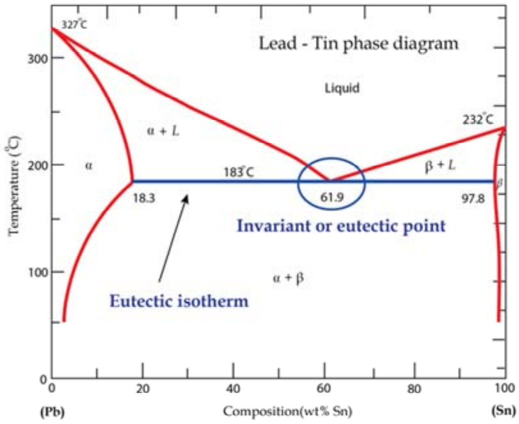
<u>Copper-Silver</u>



Binary Phase Diagrams

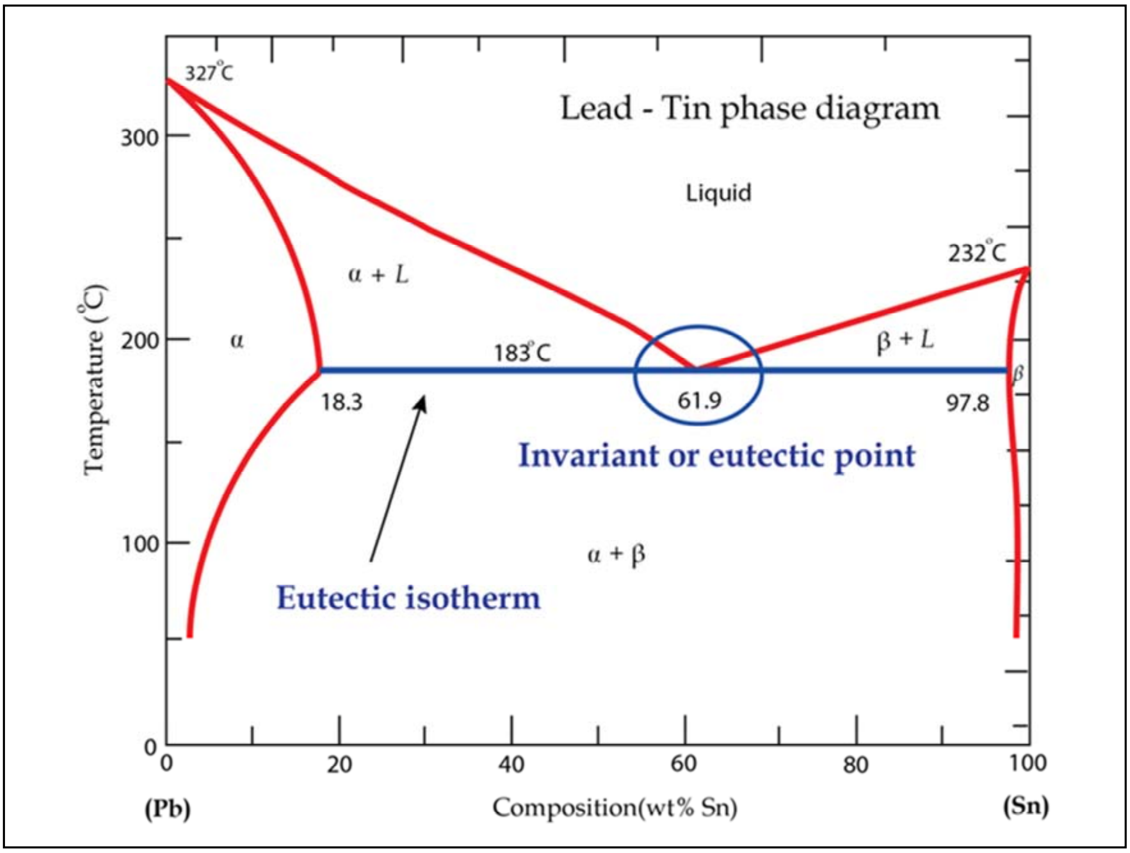
Alloys with limited solubility (Eutectic systems)

Pb-Sn



The three two-phase regions are separated by a horizontal line corresponding to the eutectic temperature.

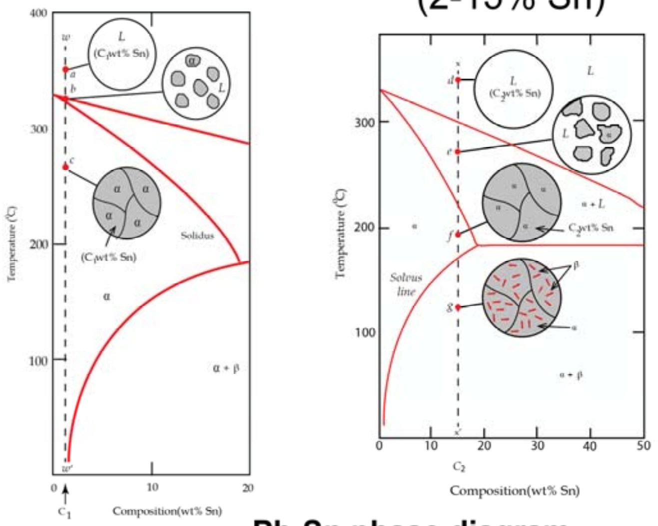
The eutectic point gives the composition that remains liquid until the eutectic temperature.


Lead - Tin phase diagram
Liquid
327°C
232°C
α + L
α
β + L
β
183°C
18.3
61.9
97.8
Invariant or eutectic point
α + β
Eutectic isotherm
Temperature (°C)
300
200
100
0
0
20
40
60
80
100
(Pb)
Composition(wt% Sn)
(Sn)

Microstructure Formation in Eutectic Alloys

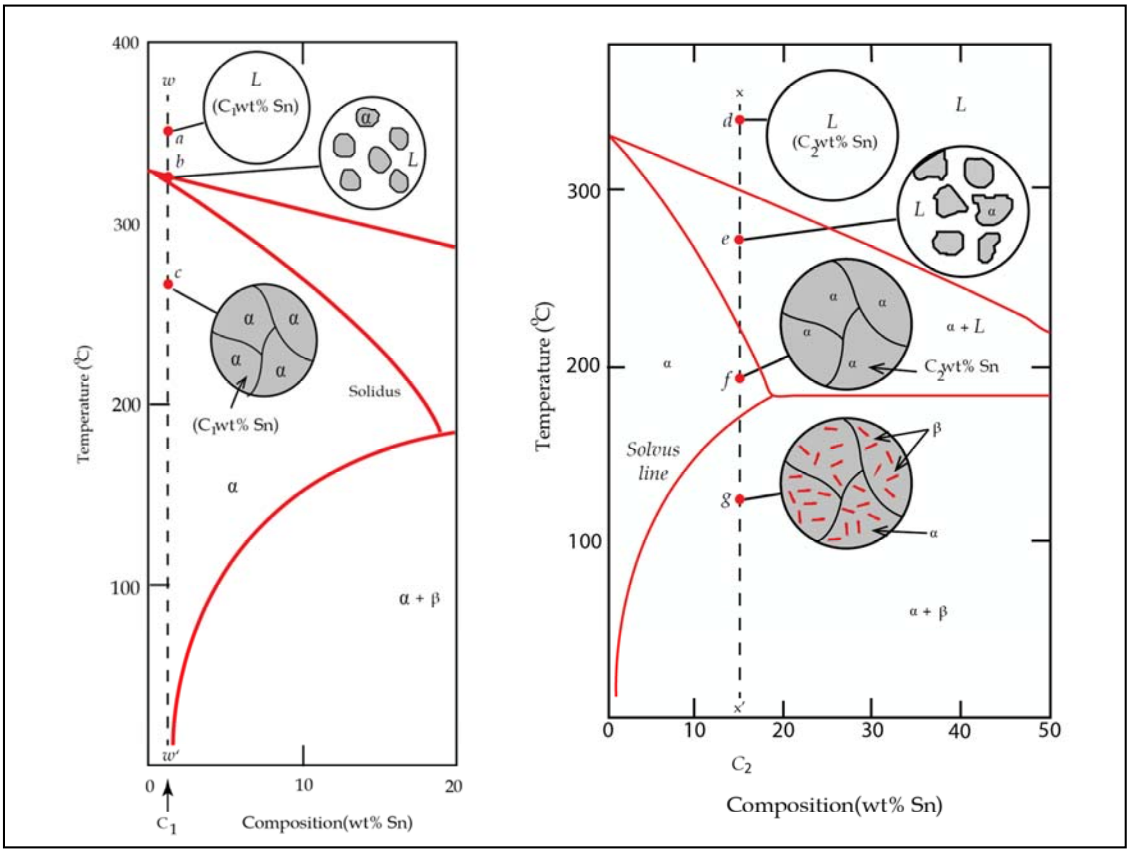
Lead-rich alloy (0-2% Sn)

Lead-rich alloy (2-15% Sn)



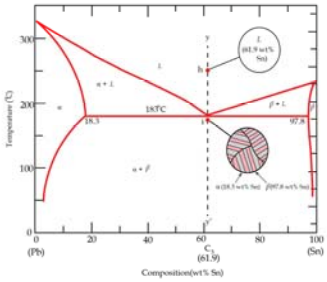
Pb-Sn phase diagram

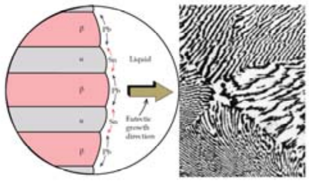
At higher Sn contents, the β phase nucleates as the α solid solubility is exceeded upon crossing the solvus line.


400
300
200
100
Temperature (°C)
w
a
b
c
L
(C_1wt% Sn)
α
L
α
α
α
α
(C_1wt% Sn)
Solidus
α
α + β
w'
0
10
20
C_1
Composition(wt% Sn)
300
200
100
Temperature (°C)
x
d
e
f
g
L
(C_2wt% Sn)
L
L
α
α
α
α
α
α + L
C_2wt% Sn
α
Solvus
line
β
α
α + β
x'
0
10
20
30
40
50
C_2
Composition(wt% Sn)

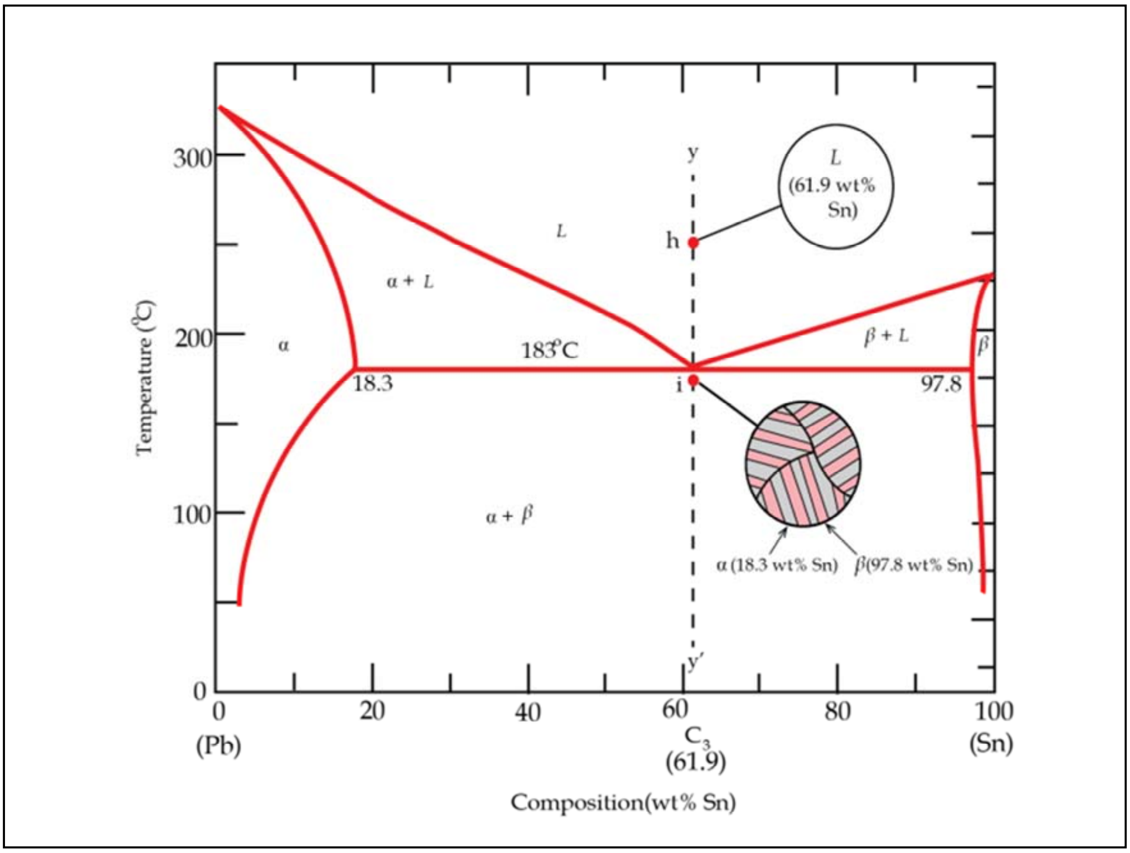
Microstructure Formation in Eutectic Alloys

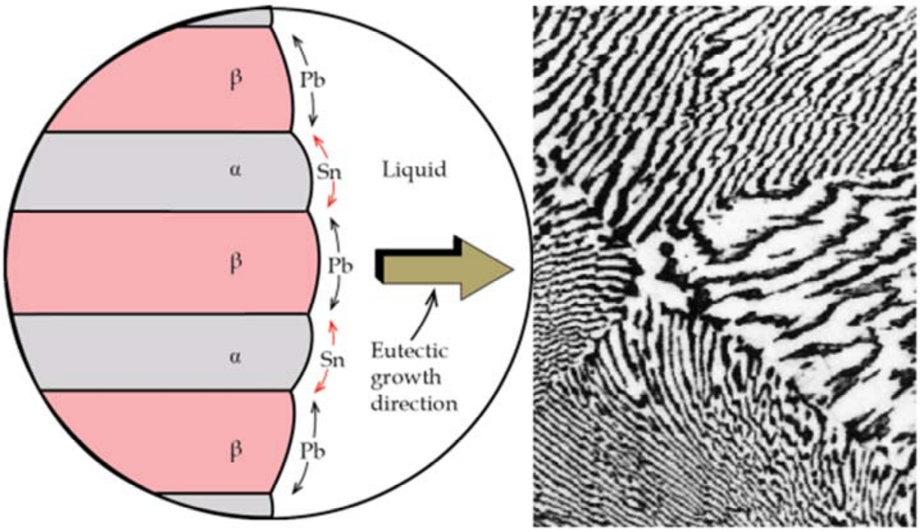
Lead-Tin alloy at eutectic point





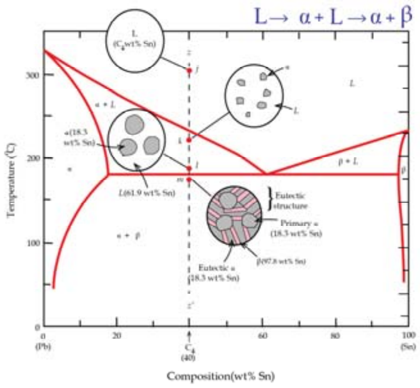
- Simultaneous formation of α and β phases results in a layered (lamellar) microstructure that is called a *eutectic structure*.
- Dark layers are lead-rich α phase and the lighter layers are tin-rich β phase.

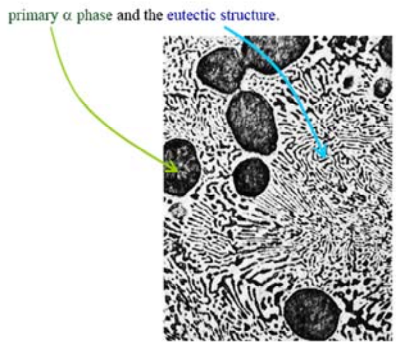

300
200
100
0
Temperature (°C)
y
L
(61.9 wt%
Sn)
h
L
α + L
α
183°C
β + L
β
18.3
i
97.8
α + β
α (18.3 wt% Sn)
β(97.8 wt% Sn)
y′
0
(Pb)
20
40
60
C3
(61.9)
80
100
(Sn)
Composition(wt% Sn)


β
Pb
α
Sn
Liquid
β
Pb
α
Sn
Eutectic
growth
direction
β
Pb

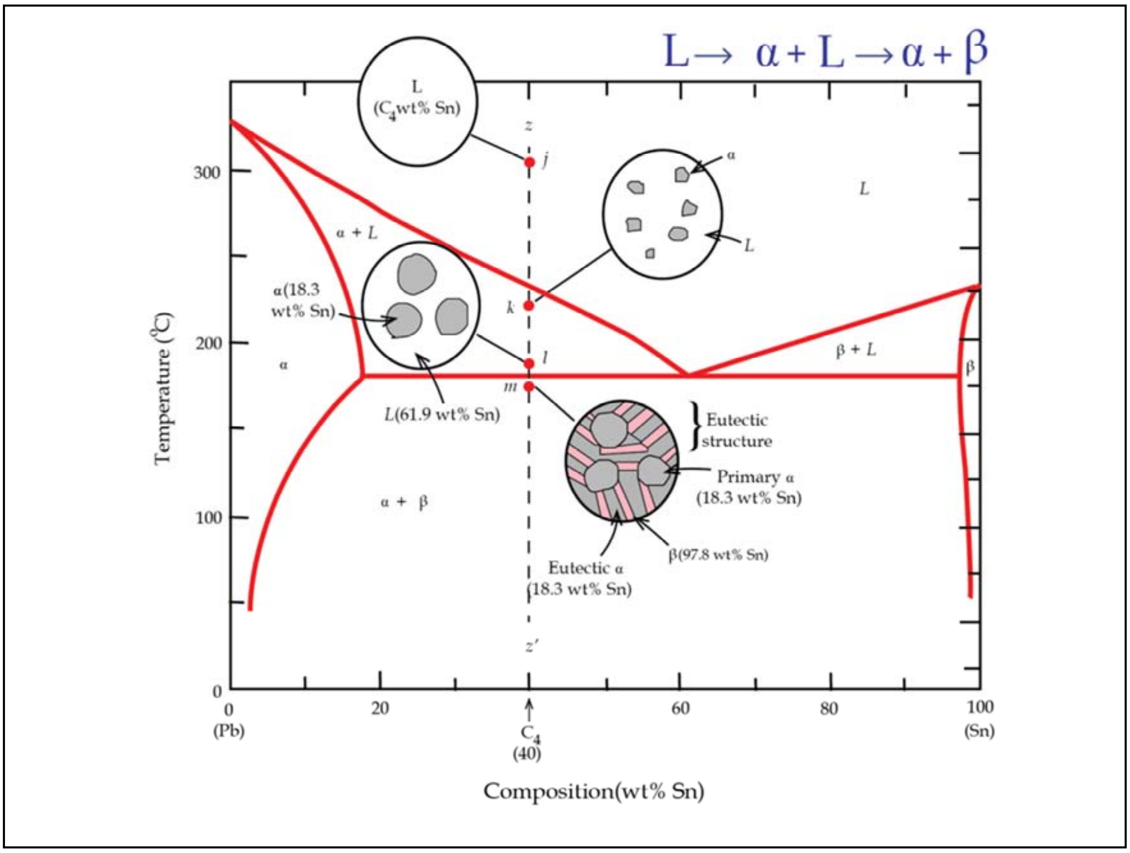
Microstructure Formation in Eutectic Alloys

Lead-Tin alloy at other than eutectic but within the range of the eutectic isotherm

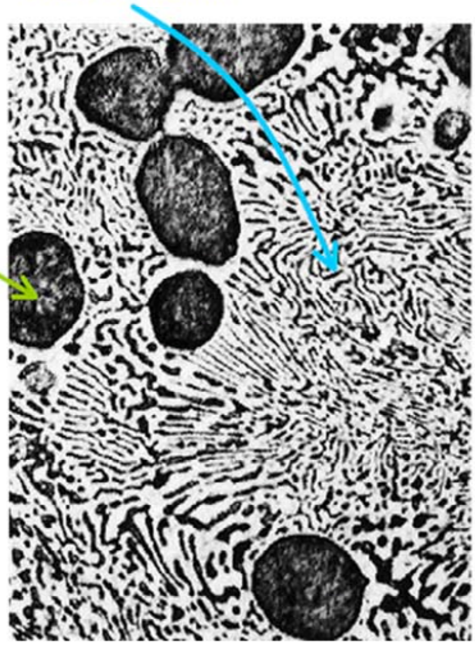




Primary α phase is formed in the α+L region, and the eutectic structure (layers of α and β phases) is formed upon crossing the isotherm.

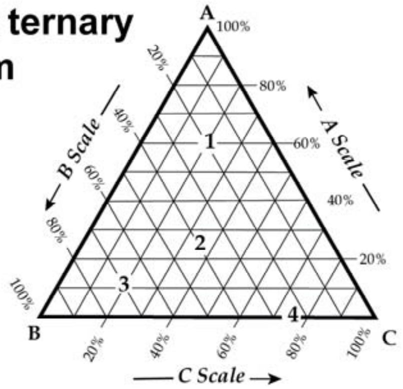

L→ α+L→α+β
L
(C4wt% Sn)
z
j
α
L
L
300
α + L
α(18.3
wt% Sn)
k
200
α
l
β + L
β
m
L(61.9 wt% Sn)
Eutectic
structure
Primary α
(18.3 wt% Sn)
α + β
100
β(97.8 wt% Sn)
Eutectic α
(18.3 wt% Sn)
z′
Temperature (°C)
0
0
(Pb)
20
C4
(40)
60
80
100
(Sn)
Composition(wt% Sn)

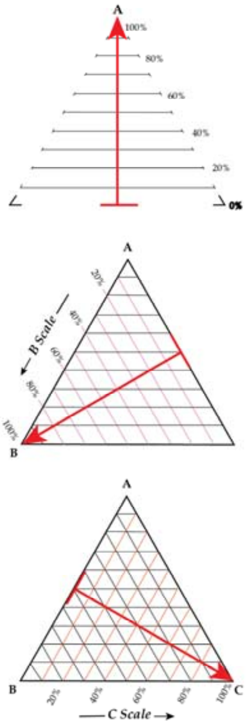
primary α phase and the eutectic structure.



Ternary Systems

How to read a ternary diagram



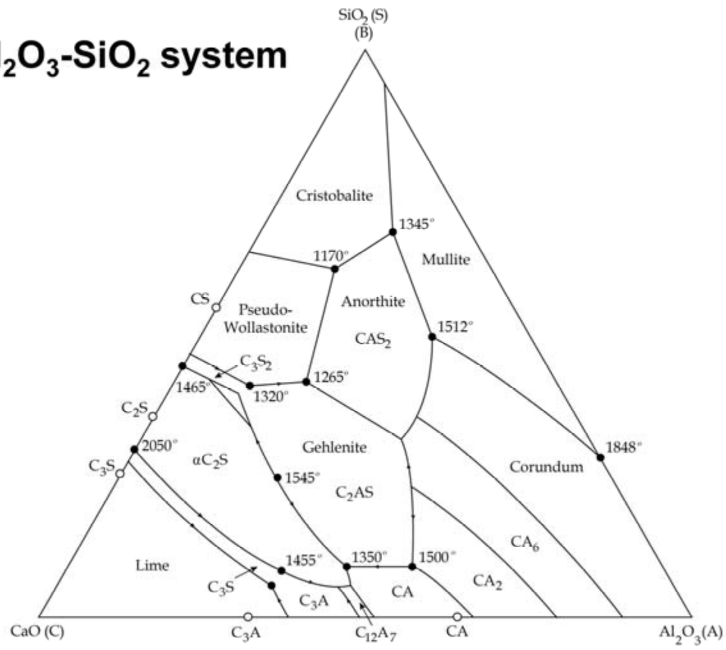


Compositions for the marked points:

1. 60% A | 20% B | 20% C = 100%
2. 25% A | 40% B | 35% C = 100%
3. 10% A | 70% B | 20% C = 100%
4. 0.0% A | 25% B | 75% C = 100%

Ternary Systems

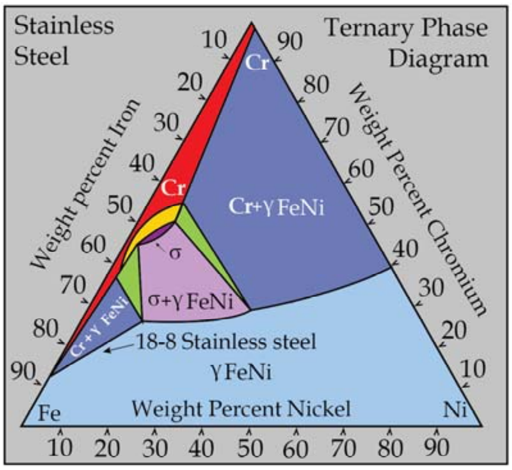
CaO-Al_2O_3-SiO_2 system



Young et al.

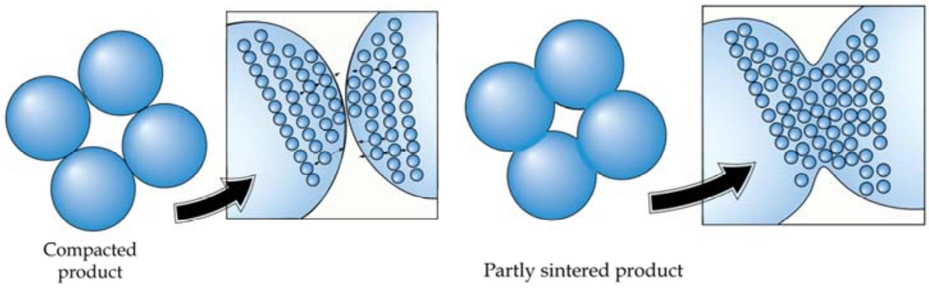
Ternary Systems

Fe-Cr-Ni system



Sintering

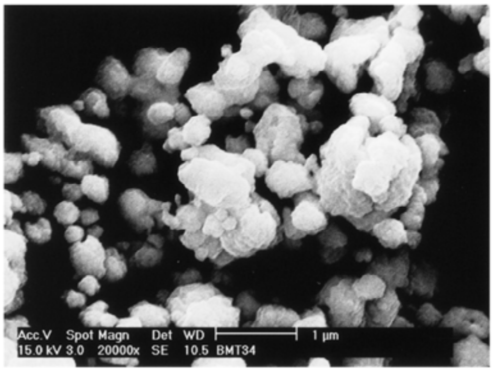
- When adjacent particles that are in close contact are heated at a temperature well below the melting point, a solid bridge or "neck" is formed between them. This is called sintering.



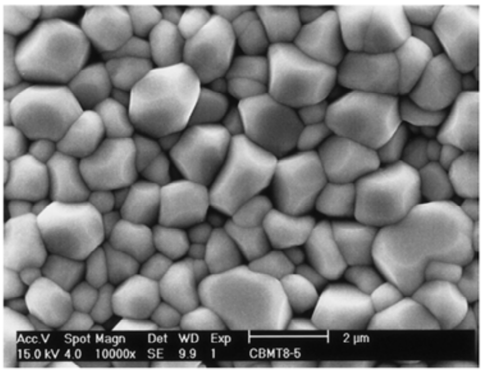
- Atoms diffuse to points of contact, creating bridges and reducing the pore size

Young et al.

Sintering



Particles of barium magnesium tantalate (BMT)

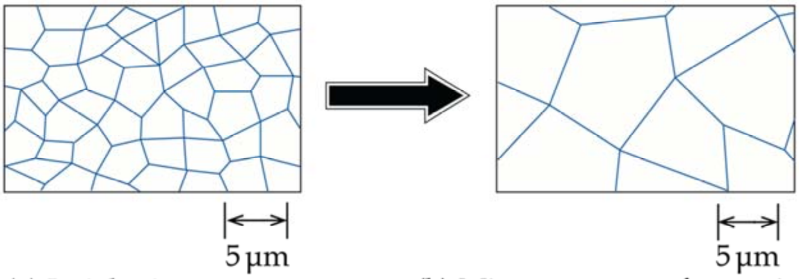


The microstructure of BMT ceramics obtained by compaction and sintering of BMT powders.

Young et al.

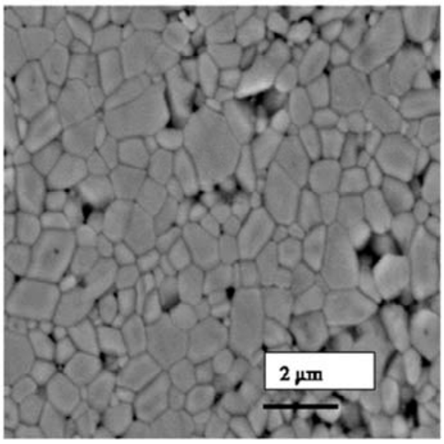
Sintering

- Sintering also involves *grain growth* (gradual adsorption of small particles into larger ones).
- Grain growth occurs when there is a movement of grain boundaries by diffusion in order to reduce the amount of grain boundary area.

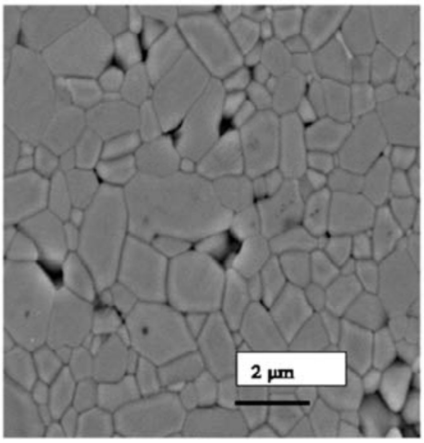


(a) Intial microstructure (b) Microstructure after grain growth

Sintering: Grain Growth



(a)

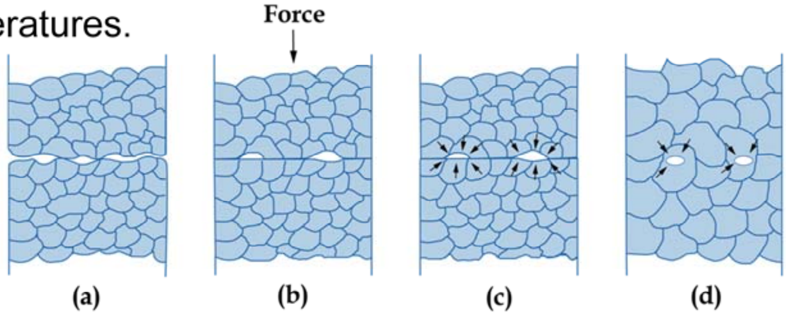


(b)

Grain growth in alumina ceramics can be seen from SEM micrographs.

Diffusion Bonding

Diffusion bonding is a joining technique in which two surfaces are pressed together at high pressures and temperatures.



The steps in diffusion bonding: (a) Initially the contact area is small; (b) application of pressure deforms the surface, increasing the bonding area; (c) grain boundary diffusion permits voids to shrink; and (d) final elimination of the voids requires volume diffusion

References

- *The Science and Technology of Civil Engineering Materials*, J.F. Young, S. Mindess, R.J. Gray & A. Bentur, Prentice Hall, 1998
- *Introduction to Properties of Materials*, D. Rosenthal, van Nostrand, 1964
- *Properties of Engineering Materials*, R.A. Higgins, Industrial Press, 1994
- *Materials Science and Engineering: A first course*, V.Raghavan, Prentice-Hall, 2004.
- *Phase diagrams*, http://www.soton.ac.uk/%7Epasr1/index.htm