Universidad
Carlos III de Madrid
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Materials Science and Engineering

TOPIC 3. Phase Diagrams I

- Basic concepts:
  - ✓ Component, phase, micro constituent.
- Unary or one component phase diagrams.
- Binary isomorphous phase diagrams.
- Gibbs Phase Rule.
- Tie line and lever rule.
- Binary eutectic systems.
- Precipitation in solid state.
- Invariant reactions.
- Intermetallic components.
- Congruent and incongruent melting.

BASIC CONCEPTS

Component

Chemical substance or compound with fixed composition that can form part of a phase or alloy. Examples: Aluminium (Al), Alumina (Al_2O_3).

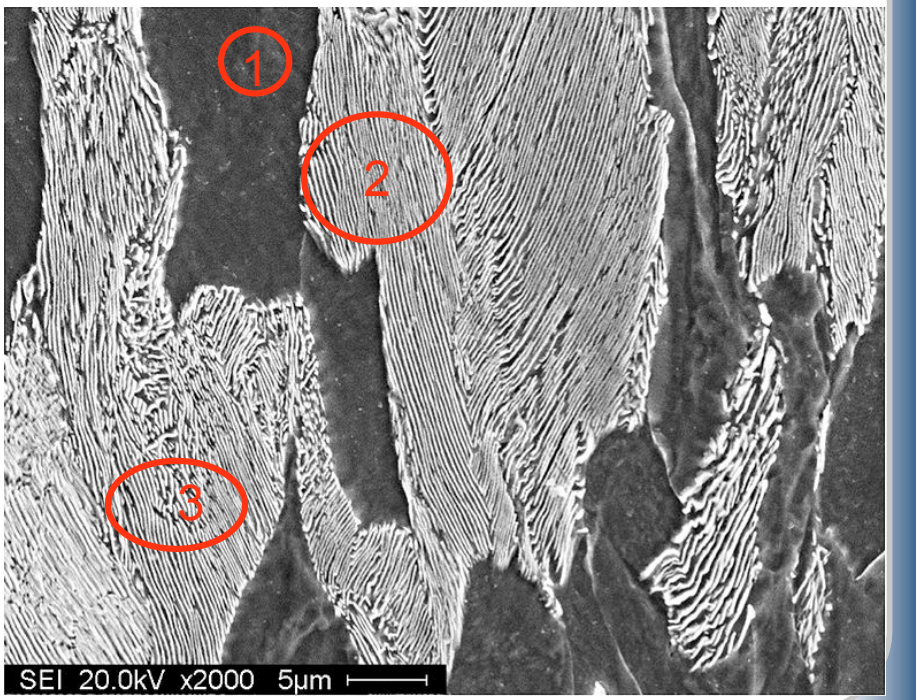
Phase

Chemically and structurally homogeneous area that forms part of the microstructure. Could be formed by one or various components. Examples: Ferrite (solid solution Fe-C with BCC structure) austenite (solid solution Fe-C with FCC structure), calcium carbonate ($CaCO_3$)

Microconstituent

Each one of different structures that can be observed on a polished surface of the material. Can be formed by one or various phases

1: Ferrite
2 and 3: pearlite (ferrite + cementite)

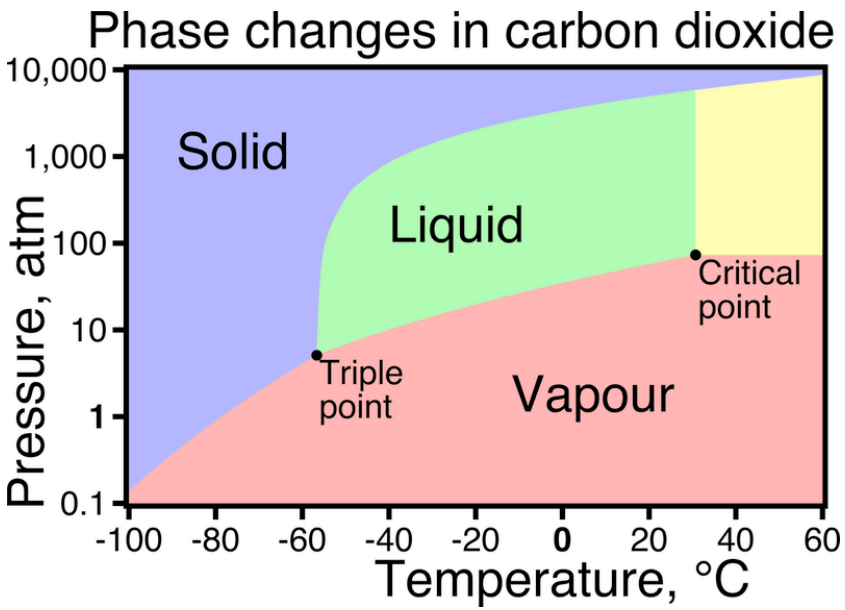


Secondary electron image of a polished and etched section of a steel helical gear. Microstructure consists of pearlite in a ferrite matrix. Etched in 3% nital. 2000X

DEFINITION OF EQUILIBRIUM PHASE DIAGRAM

Equilibrium diagram :
Map of the phases in thermodynamic equilibrium that are present in a system of materials at different pressures, temperatures and compositions.

Phase diagram of CO_2



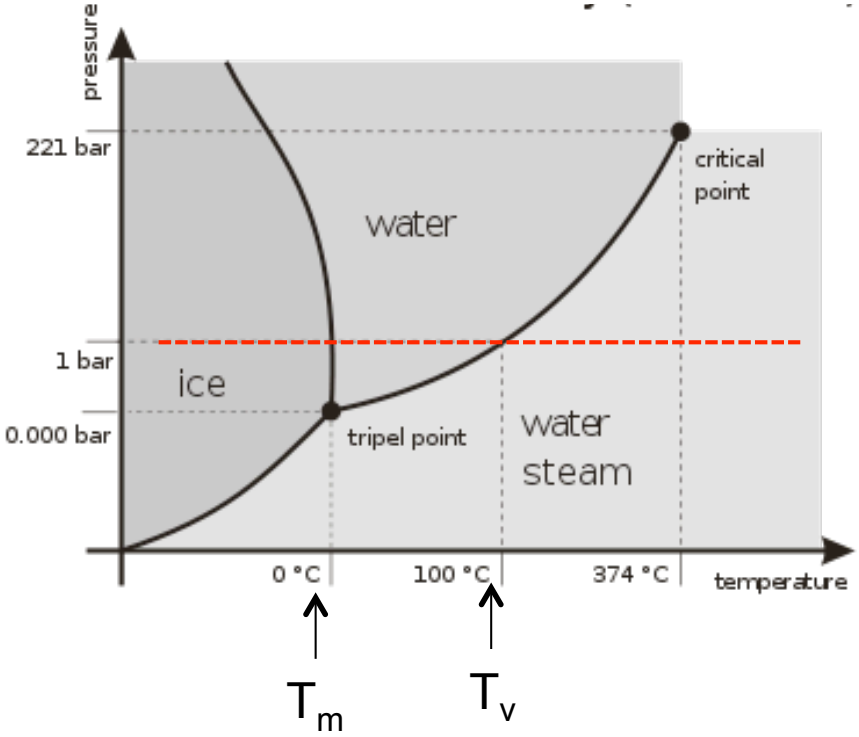
- There is no liquid CO_2 at T_{room} and ambient pressure.
- Gradient of P/T > 0, as it is in almost all substances.
- Triple-point: gas, liquid and solid are at equilibrium.
- At T below the triple point CO_2 can sublime: gas ➔ solid (dry ice)
- Above T_c = 32 °C and P_c =73 atm ➔ supercritical CO_2 fluid (used to extract caffeine from coffee)

Dry ice or card ice: solid CO_2

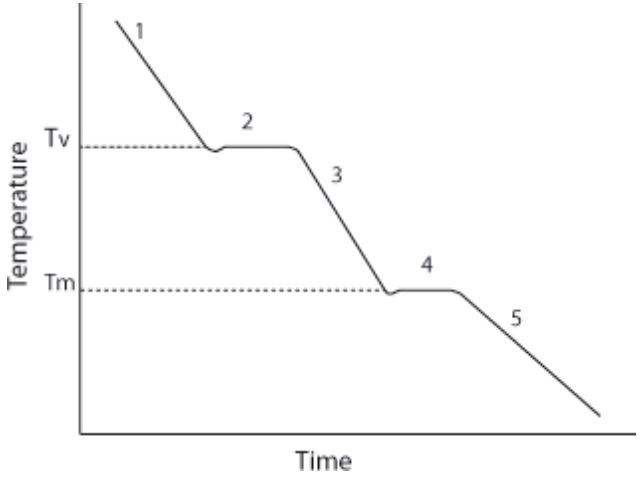
http://commons.wikimedia.org/wiki/File:Dry_Ice_Sublimation_1.jpg

UNARY OR ONE COMPONENT PHASE DIAGRAM : P-T

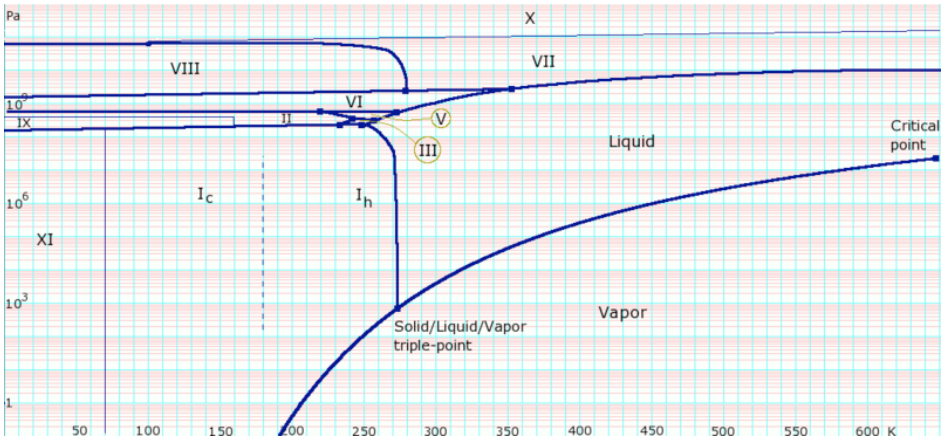
Phase diagram of water



Cooling curve for water at 1 bar



The unary phase diagram shows the P and T conditions at which thermodynamically distinct pahses can occur in equilibrium

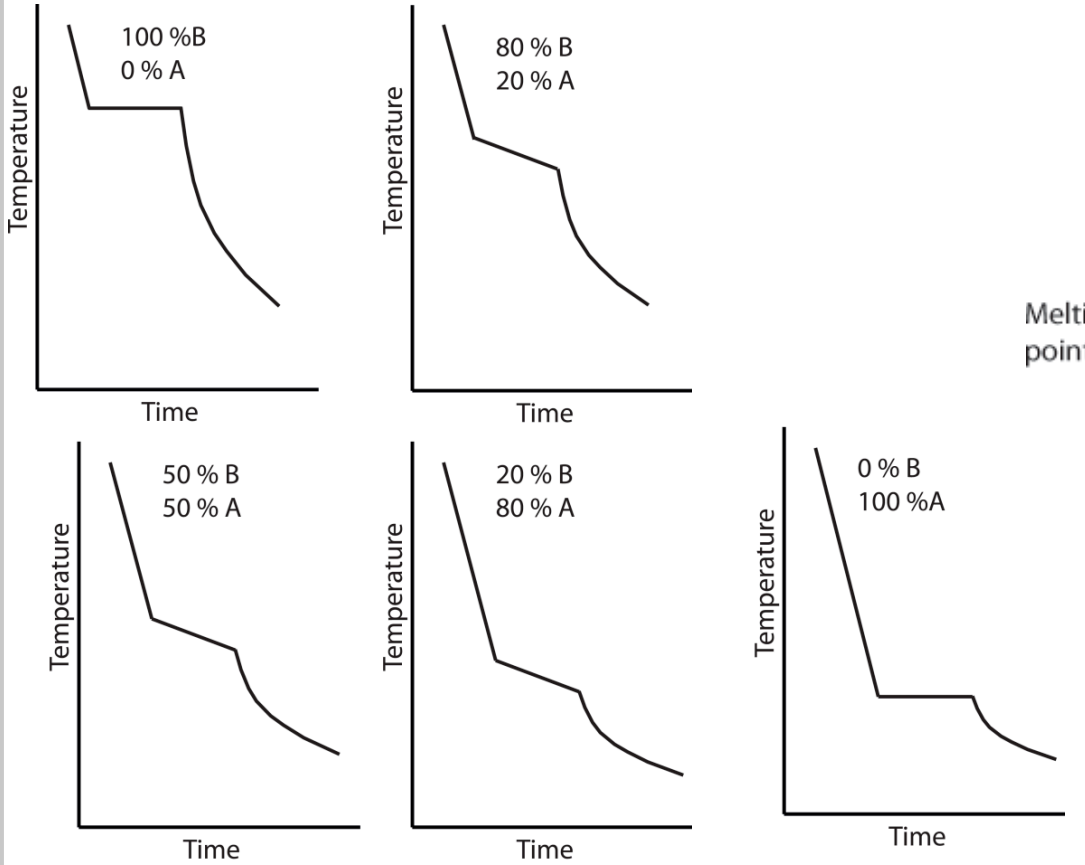


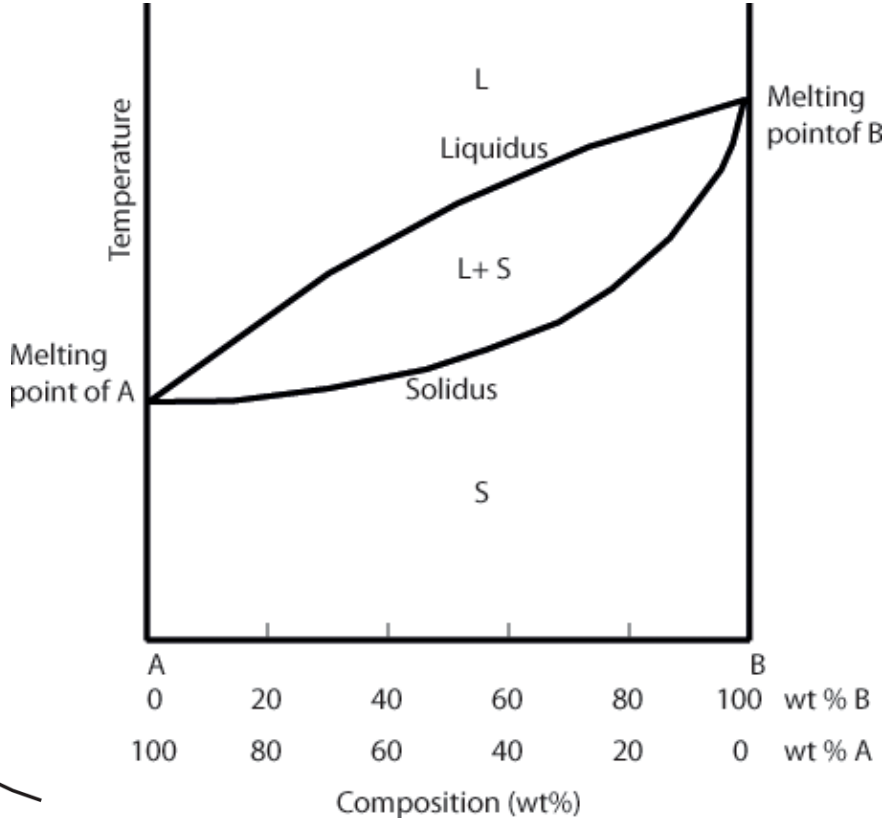
phase diagram of water

BINARY ISOMORPHOUS PHASE DIAGRAMS

SYSTEMS OF 2 COMPONENTS WITH COMPLETE SOLID SOLUBILITY

Design of a phase diagram from the cooling curves





GIBBS PHASE RULE

$$F = C - P + N$$

F = Degrees of freedom (No. of independent variables available to the system)

C = No. of components

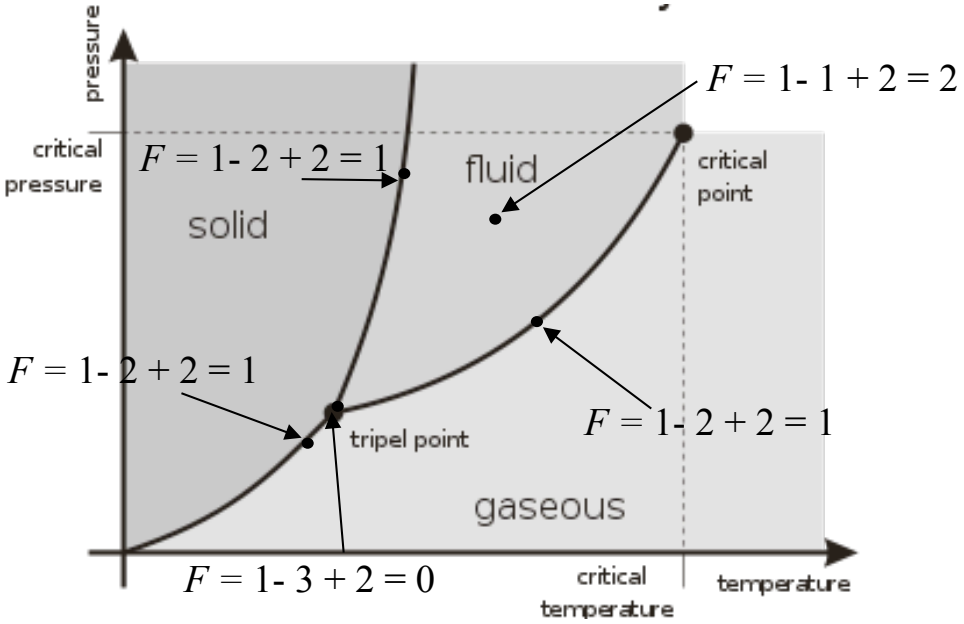
P = No. of phases

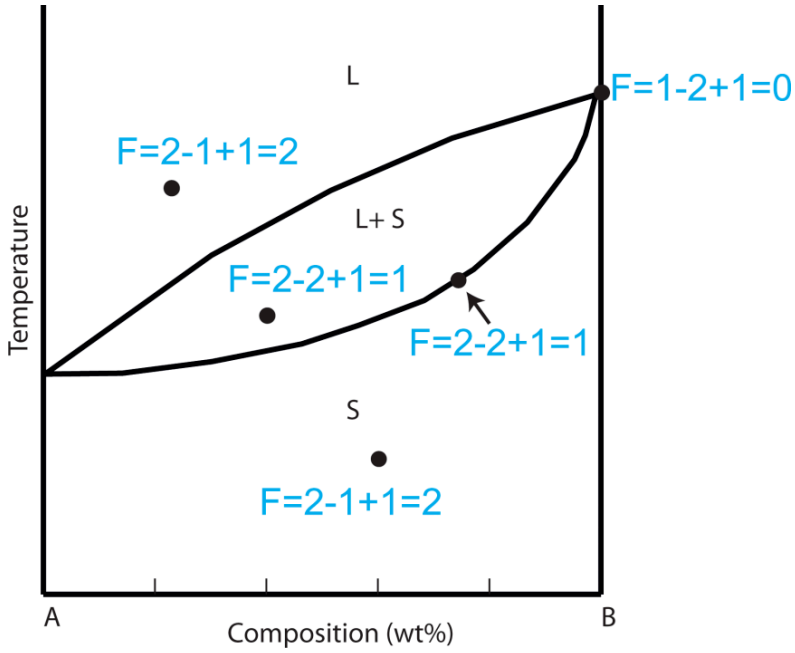
N = No. of noncompositional variables (e.g. pressure and temperature)

$$F = C - P + 2$$

For routine processing of materials, we can consider the pressure to be fixed at 1atm:

$$\Rightarrow F = C - P + 1$$





BINARY ISOMORPHOUS PHASE DIAGRAMS

Complete Solid Solubility

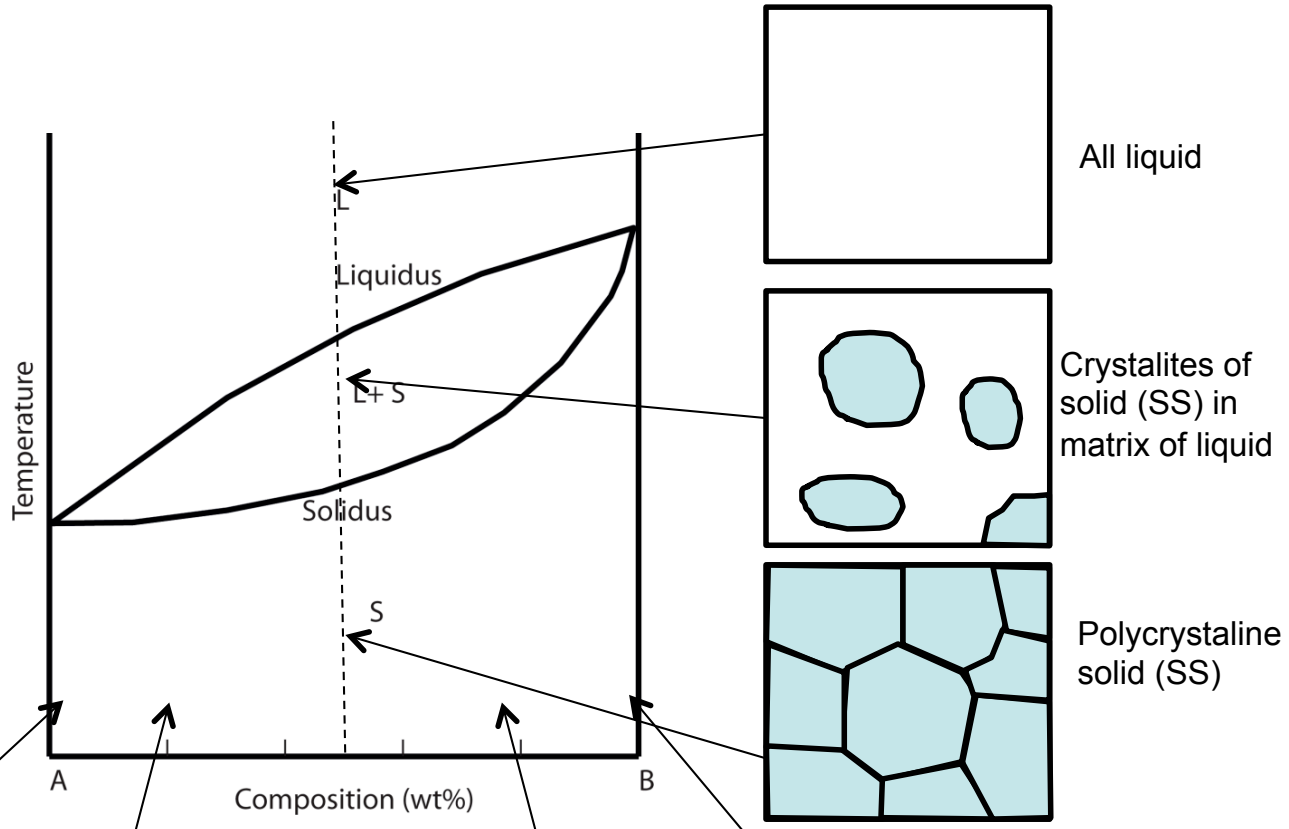
Polycrystalline single phase material.

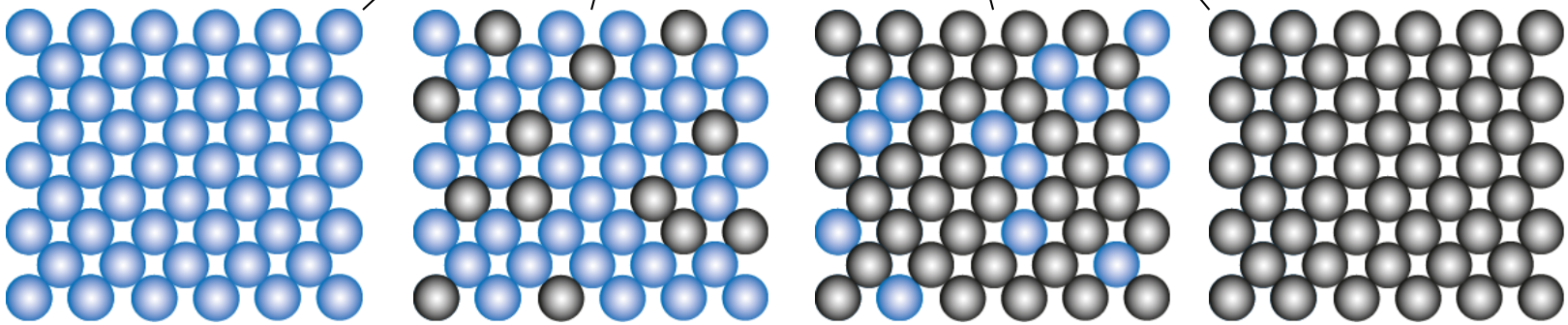
Its microstructure is not different from that of the pure metal.

When solute is added, $\mathbf{T_m}$ is modified

Complete solubility in solid state.

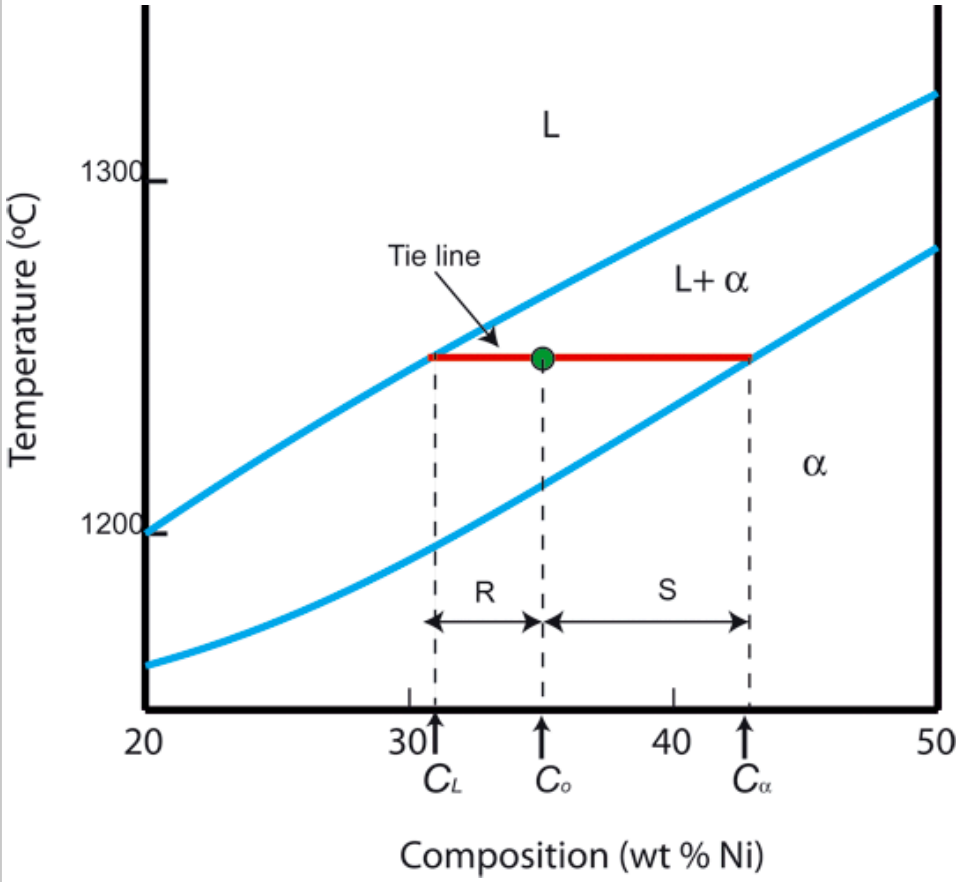
The alloy **does not solidify at a constant temperature** but at a range of temperatures





TIE LINE AND LEVER RULE

- Determination of Phase composition: Tie line
- Determination of Phase Amounts: Lever rule



W_L= fraction of liquid phase
W_α= fraction of α phase

Phase composition (Tie Line):

- Intersections of the tie line with phase boundaries
- Composition of the respective phases is given by the composition axis

LEVER RULE

Determination of Phase Amounts

- The fraction of each phase is computed by taking the length of the tie line from the overall alloy composition to the phase boundary of the *other* phase, and diving by the total line length

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

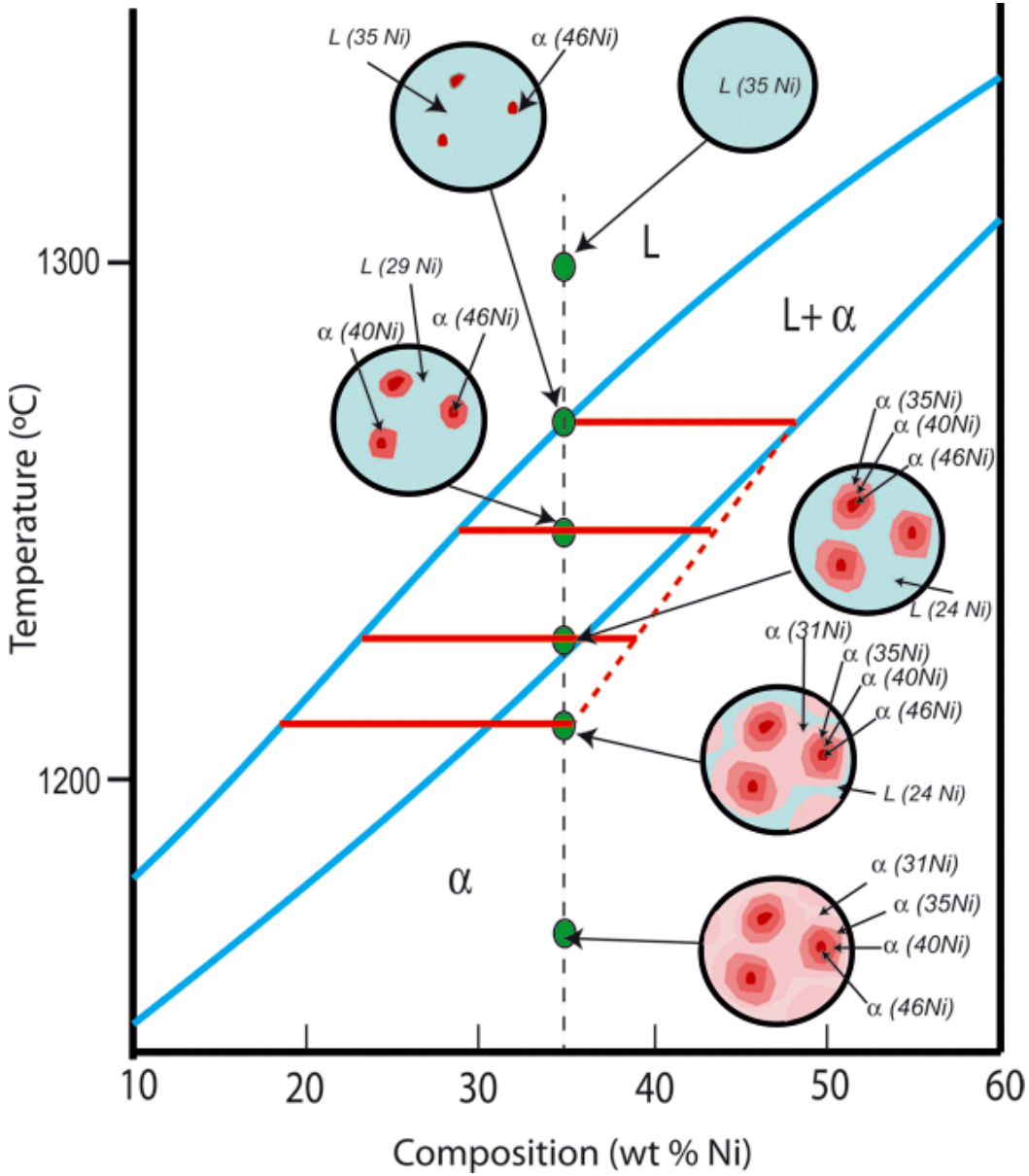
$$W_\alpha = \frac{R}{R+S} = \frac{C_0 - C_L}{C_\alpha - C_L}$$

BINARY ISOMORPHOUS PHASE DIAGRAMS

Non-equilibrium solidification

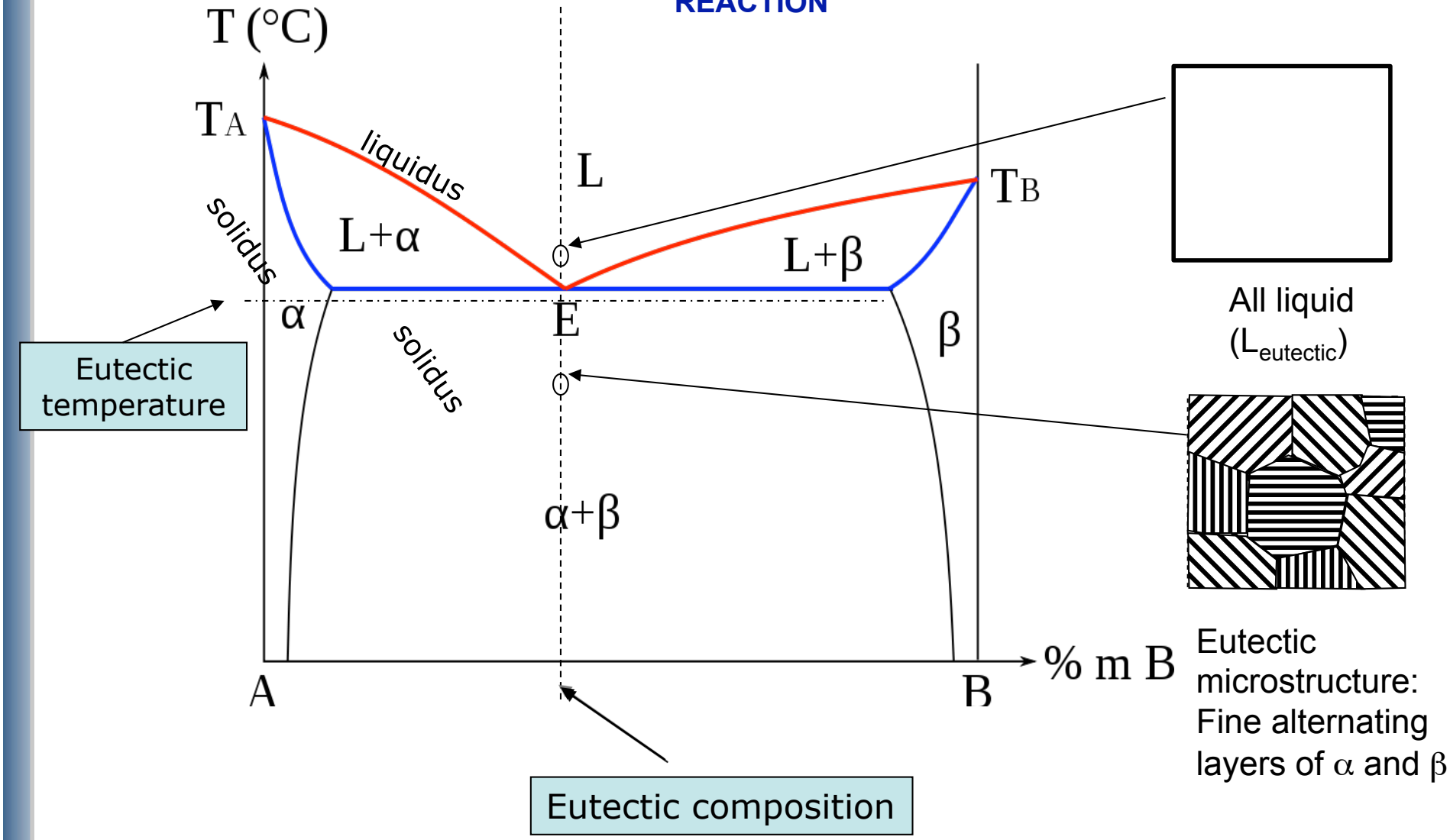
Microstructures of heterogeneous composition are produced ⇒ MICRO**segregation** (or cored structure)

Microsegrgation (or coring) can be eliminated with homogenization heat treatment at T below solidus (Example: $T_{TT} < T_7$). During heat treatment solid state diffusion occurs



BINARY EUTECTIC SYSTEMS

SYSTEMS OF 2 COMPONENTS WITH PARTIAL SOLID SOLUBILITY AND AN INVARIANT EUTECTIC REACTION

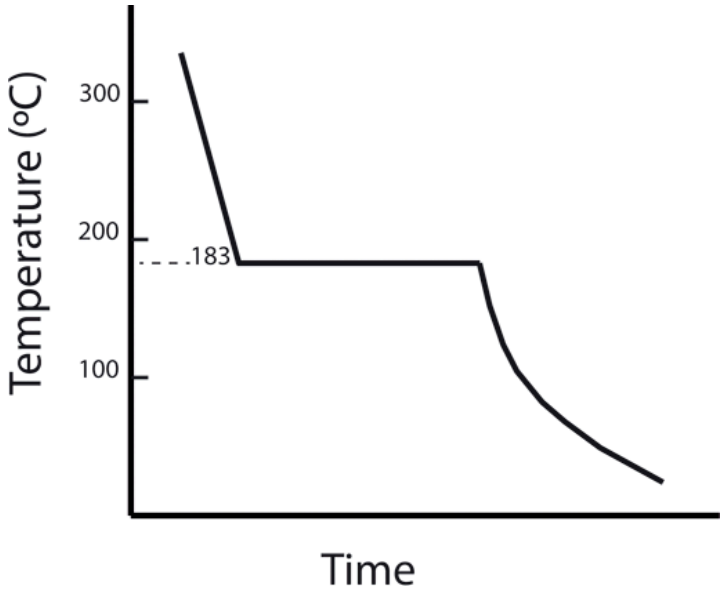


BINARY EUTECTIC SYSTEMS

INVARIANT REACTIONS: They are produced at a fixed composition and temperature for a given system, and the result also remains fixed

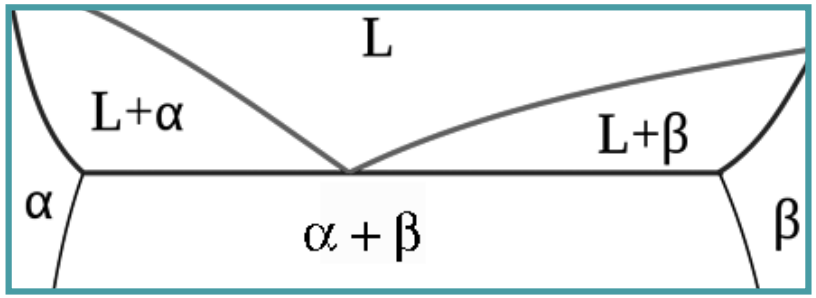
In a system of two partially soluble components a solidification reaction is produced at a fixed composition and temperature with a profile of temperature gradient similar to pure solids.

Cooling curve at eutectic Temperature



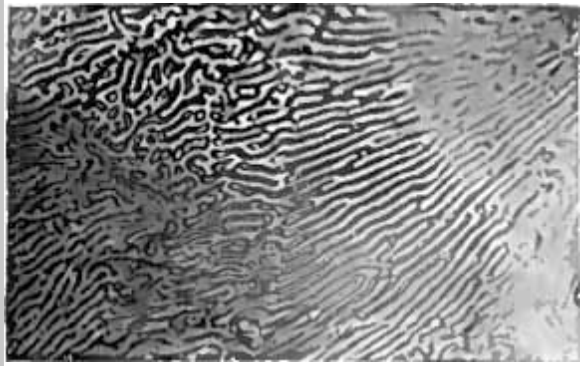
Eutectic reaction

$$L \rightarrow \alpha + \beta$$

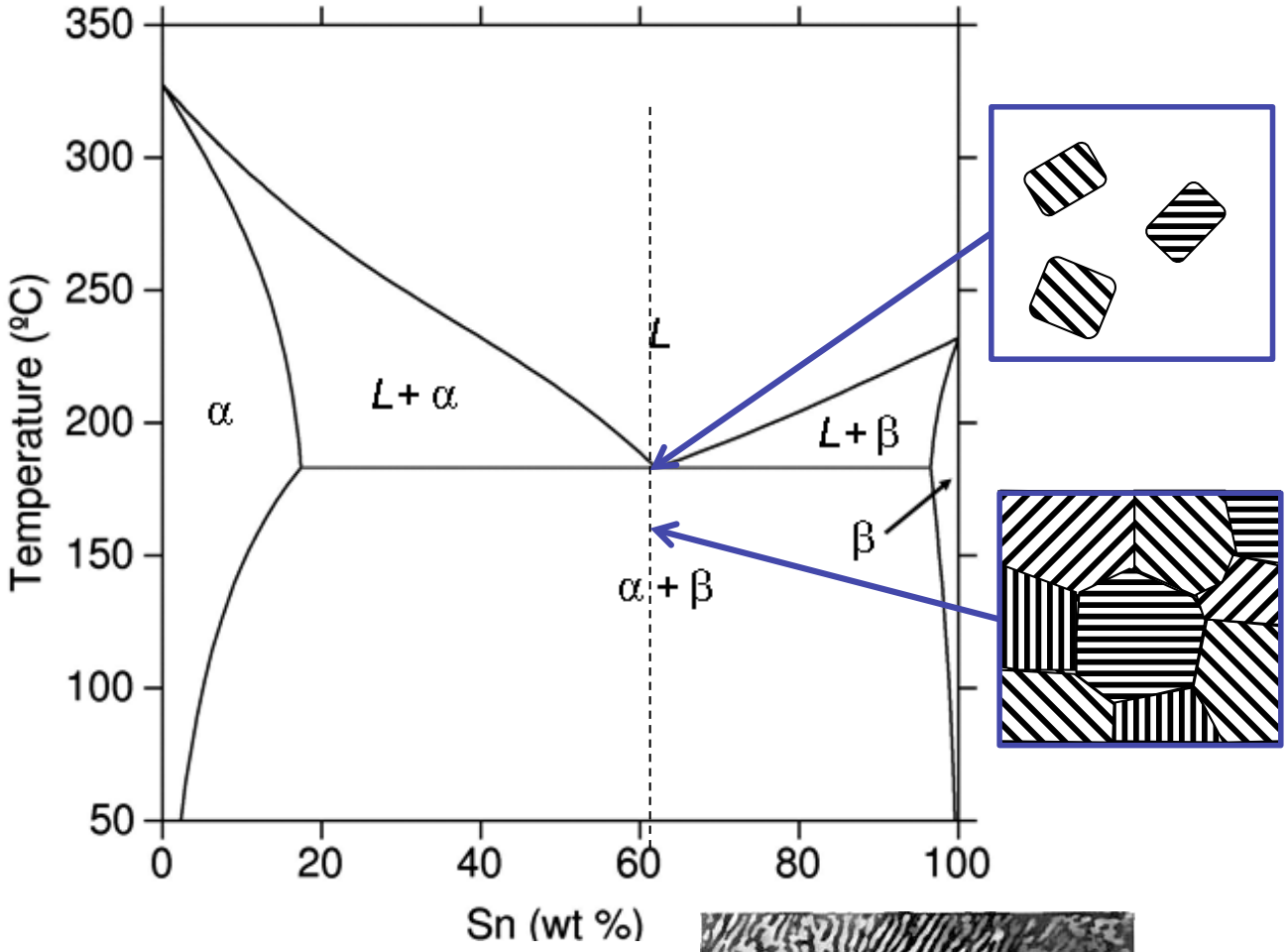


BINARY EUTECTIC SYSTEMS

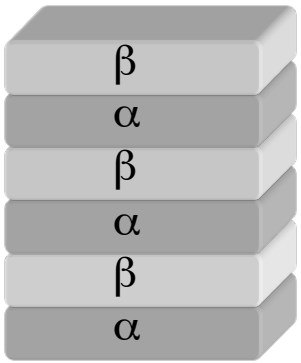
Eutectic reaction and microstructure

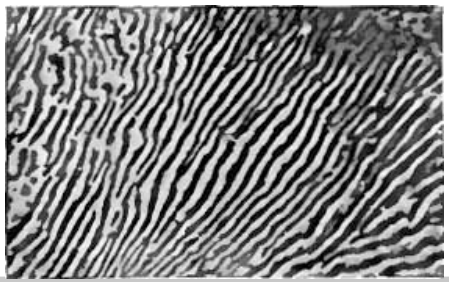


Photomicrograph of lead-tin alloy (eutectic). Lead-tin eutectic. Magnified 750 diameters.



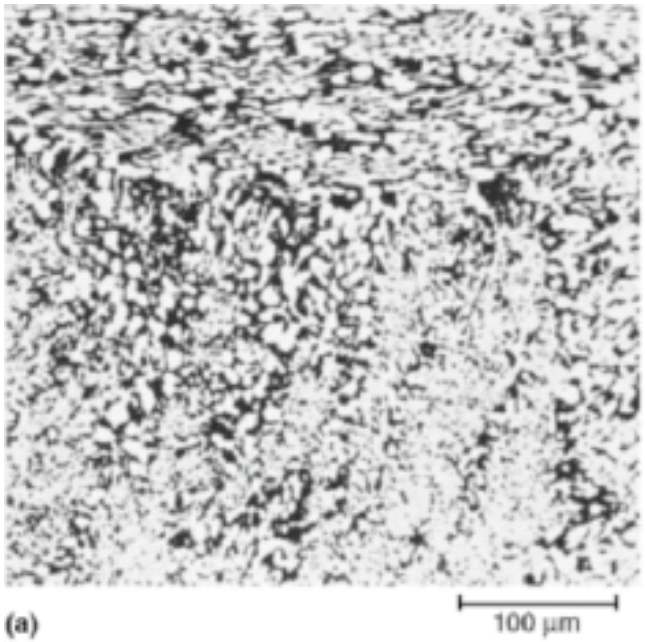
Eutectic product

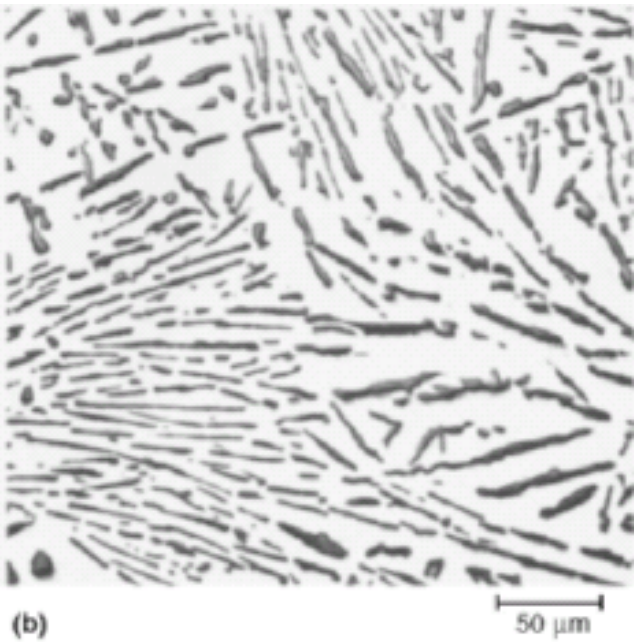


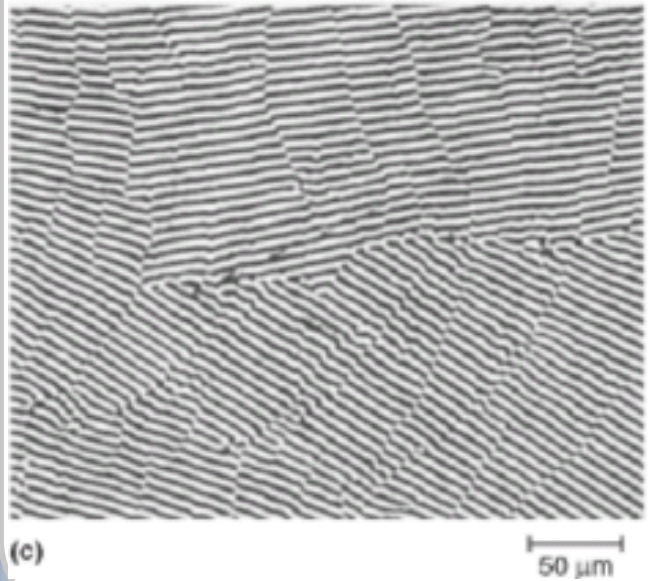


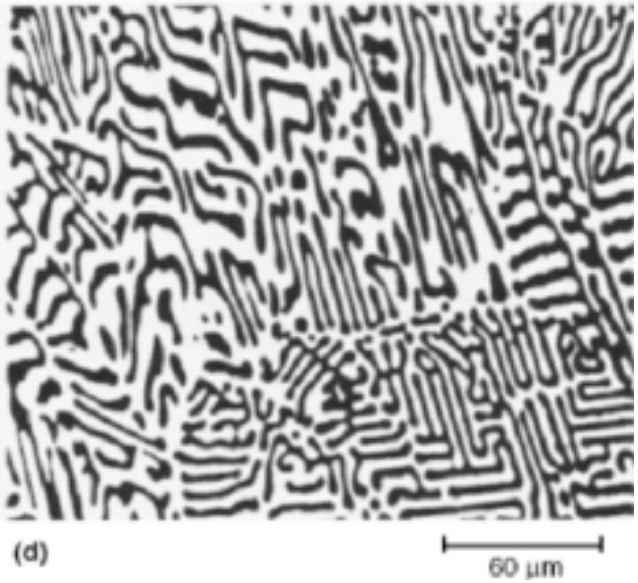
Photomicrograph of steel. Pearlite, steel (carbon about 1%) forged and annealed at 800° C. Magnified 1000 diameters

BINARY EUTECTIC SYSTEMS









a) Sn-50%In. globules of tin-rich intermetallic phase (light) in a matrix of dark indium-rich intermetallic phase.

b) Al-13%Si. Acicular structure consisting of short, angular particles of silicon (dark) in a matrix of aluminum.

c) Al-33%Cu. Lamellar structure consisting of dark platelets of $CuAl_2$ and light platelets of aluminum solid solution

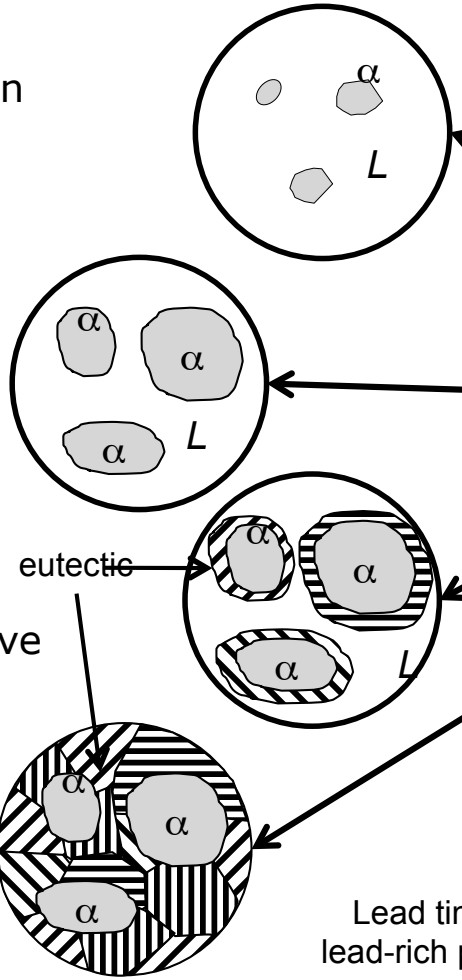
d) Mg-37%Sn. Lamellar structure consisting of Mg_2Sn "Chinese script" (dark) in a matrix of magnesium solid solution.

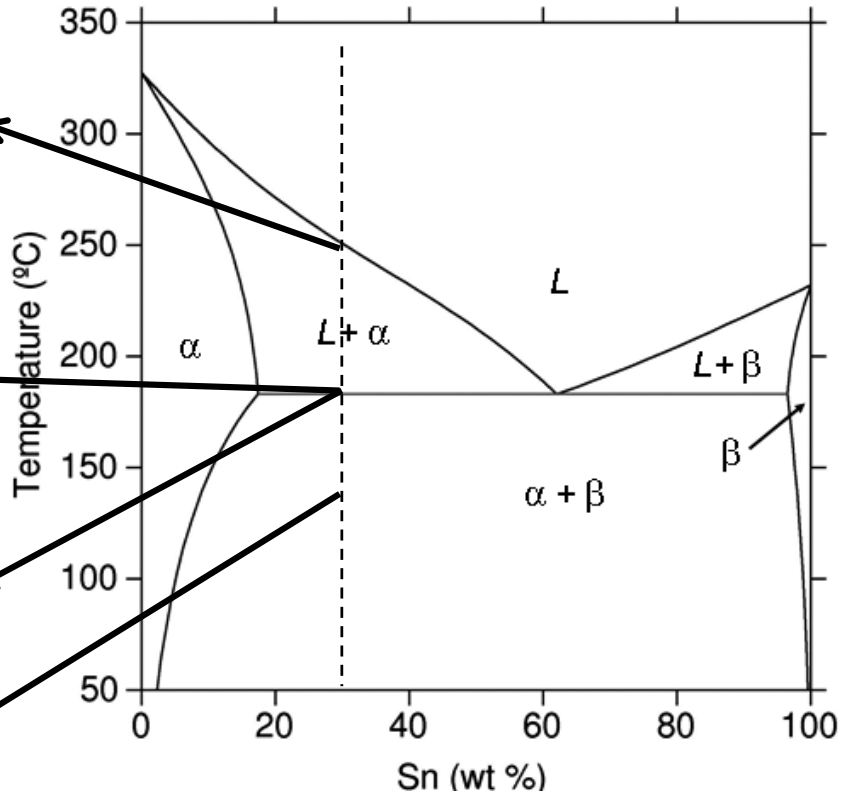
Metallography and Microstructures, Vol 9, *ASM Handbook, ASM* International,

BINARY EUTECTIC SYSTEMS

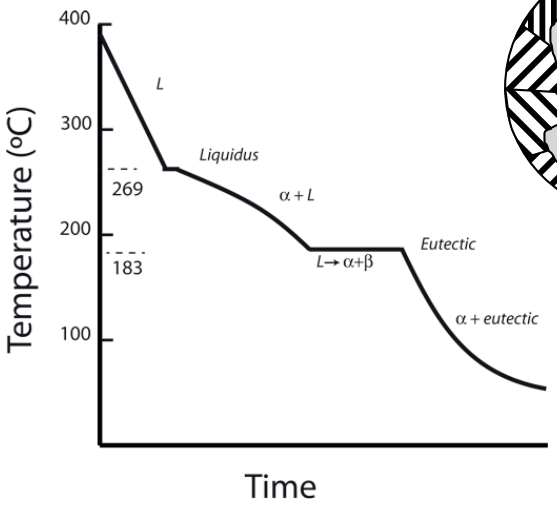
Hypo-Eutectic composition

Microstructure:
primary α and eutectic micoconstituent



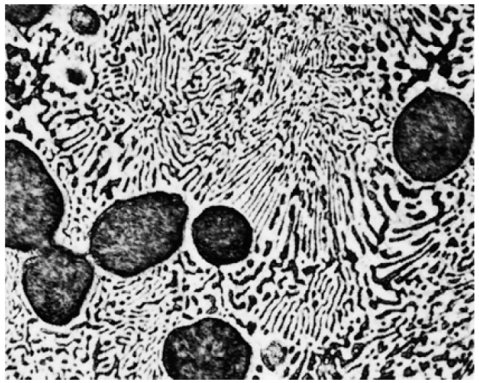


Hypo-Eutectic cooling curve



Lead tin alloy 50 wt% Pb. primary lead-rich phase (large dark regions) within a lamellar eutectic structure consisting of a tin-rich β phase (light layers) and a lead-rich α phase (dark layers).

Metallography and Microstructures, Vol 9, *ASM Handbook, ASM* International,

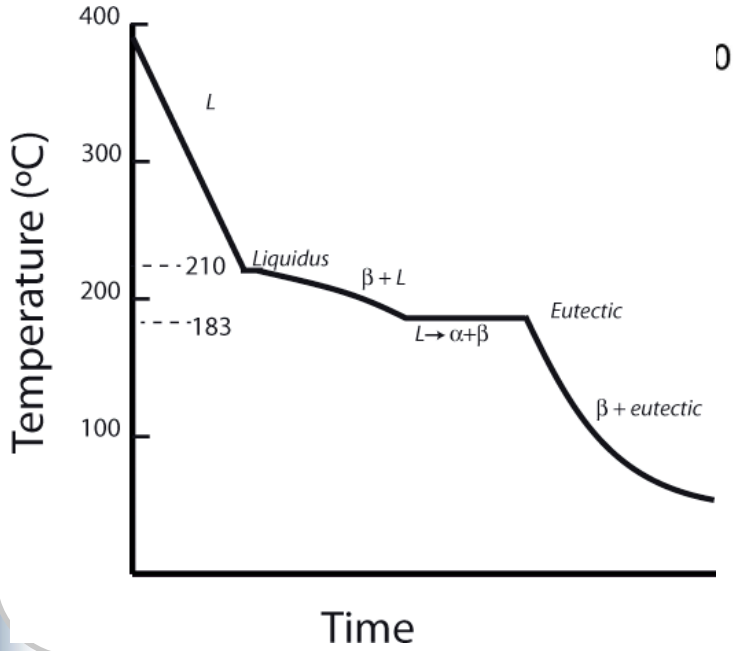


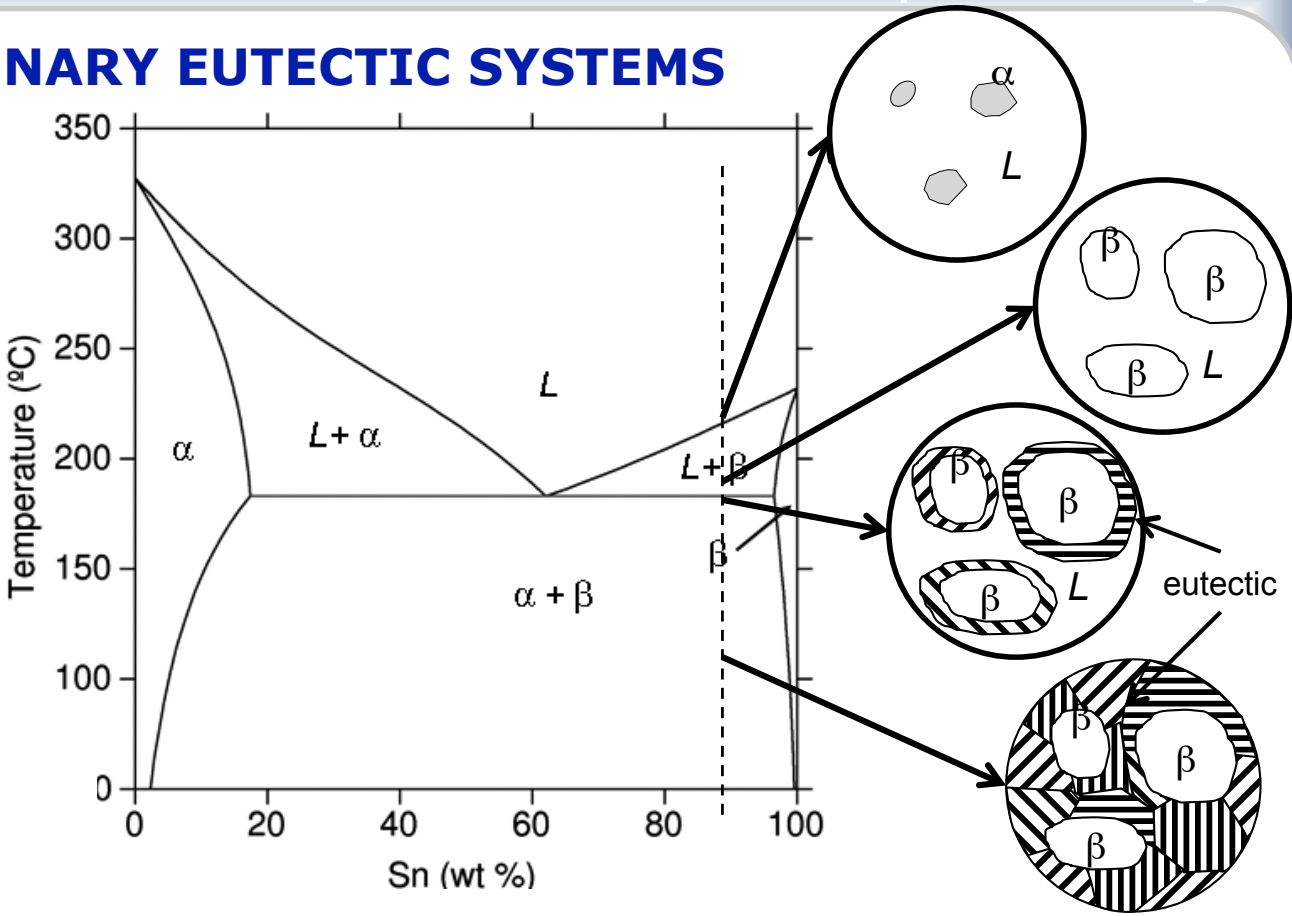
BINARY EUTECTIC SYSTEMS

Hyper-Eutectic compositions

Microstructure:
primary β and eutectic micoconstituent

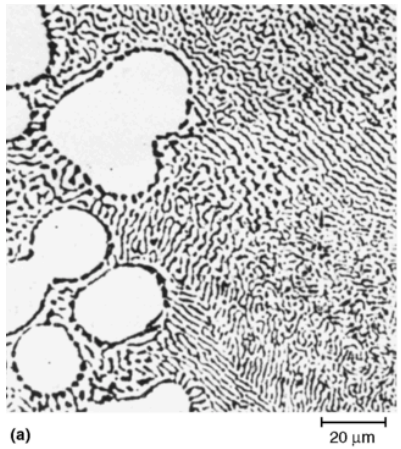
Hyper-Eutectic cooling curve



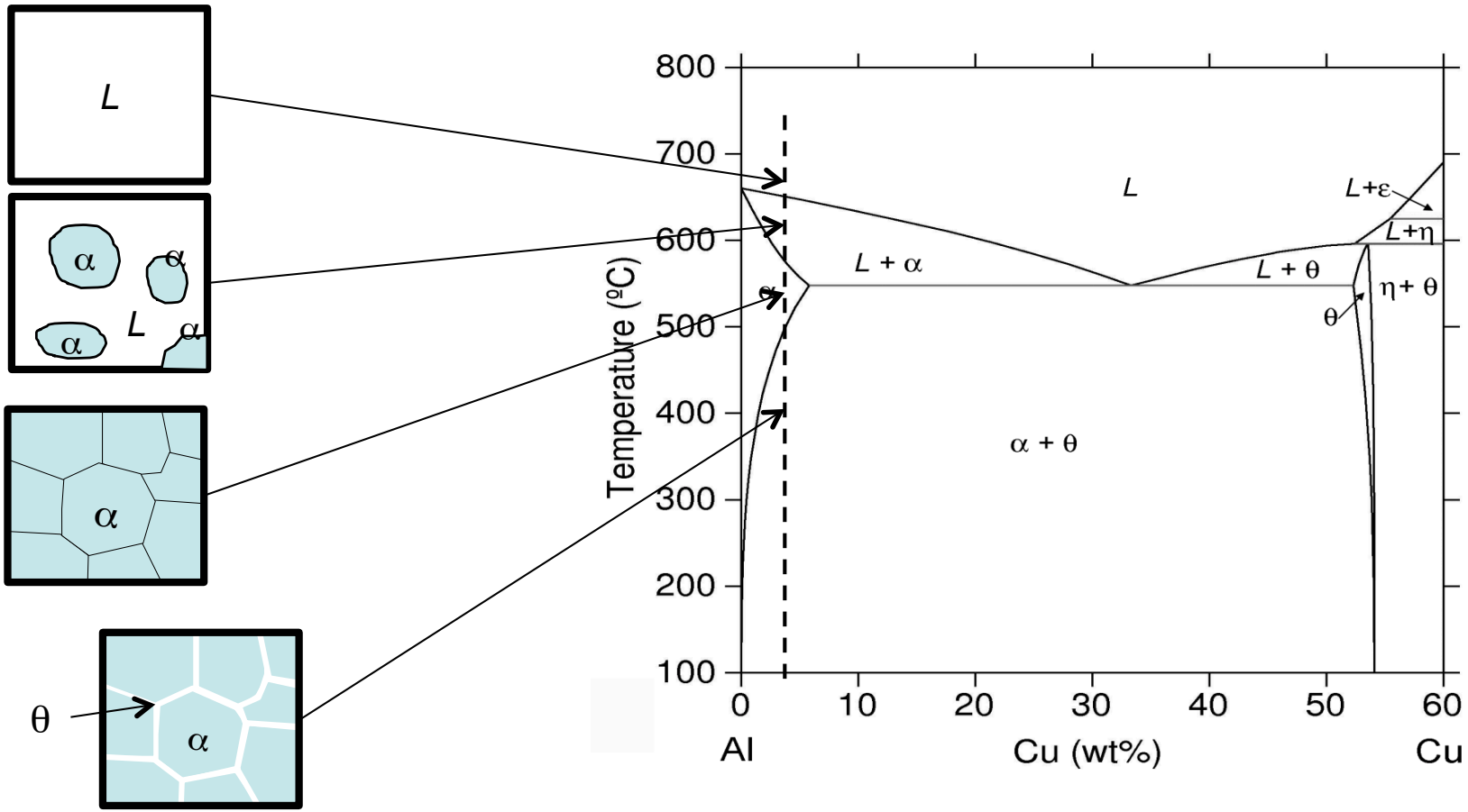


Sn-30Pb hypoeutectic alloy showing particles of tin-rich solid solution in a matrix of tin-lead eutectic.

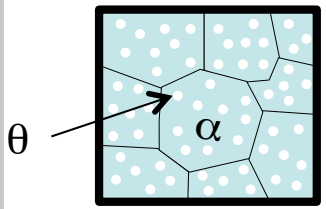
Metallography and Microstructures, Vol 9, *ASM Handbook, ASM* International,



SOLID STATE PRECIPITATION



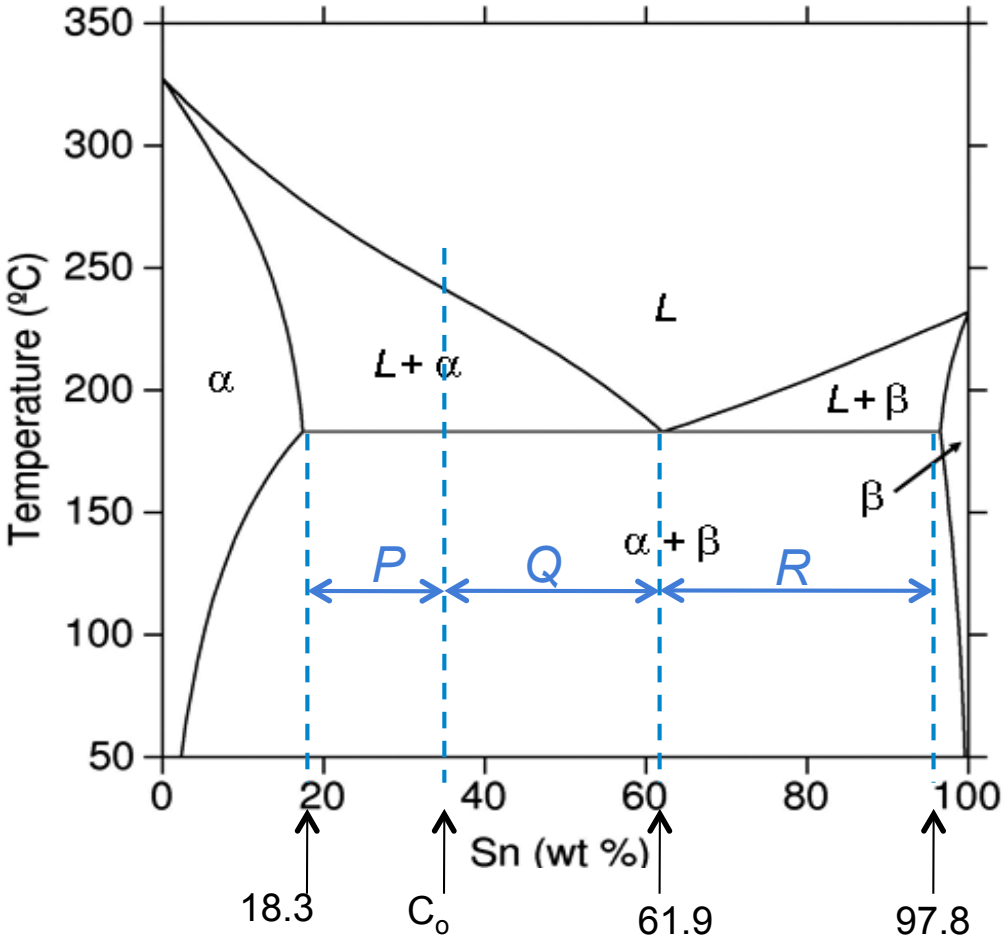
θ phase precipitates at grain boundaries (typical)



Uniform dispersion of θ phase precipitates can be achieved with a precipitation hardening heat treatment

θ phase precipitates uniformly (ideal)

LEVER RULE IN BINARY EUTECTIC PHASE DIAGRAMS



$$W_e = W_L = \frac{P}{P+Q}$$

$$W_{\alpha'} = \frac{Q}{P+Q}$$

$$W_{\alpha} = \frac{Q+R}{P+Q+R}$$

$$W_{\beta} = \frac{P}{P+Q+R}$$

W_e = fraction eutectic microconstituent
W_L = fraction of liquid phase
$W_{\alpha'}$ = fraction of α' phase (primary α)
W_{α} = *total* fraction of α (primary α + α in eutectic)
W_{β} =fraction of β phase (total)

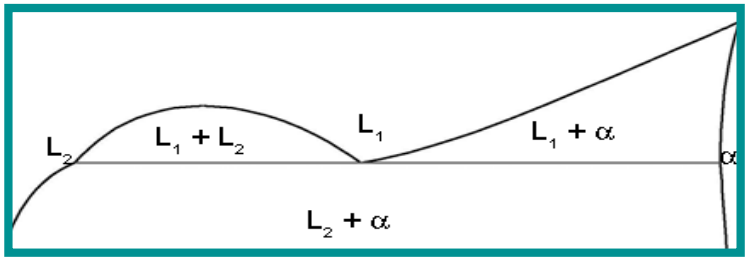
INVARIANT REACTIONS

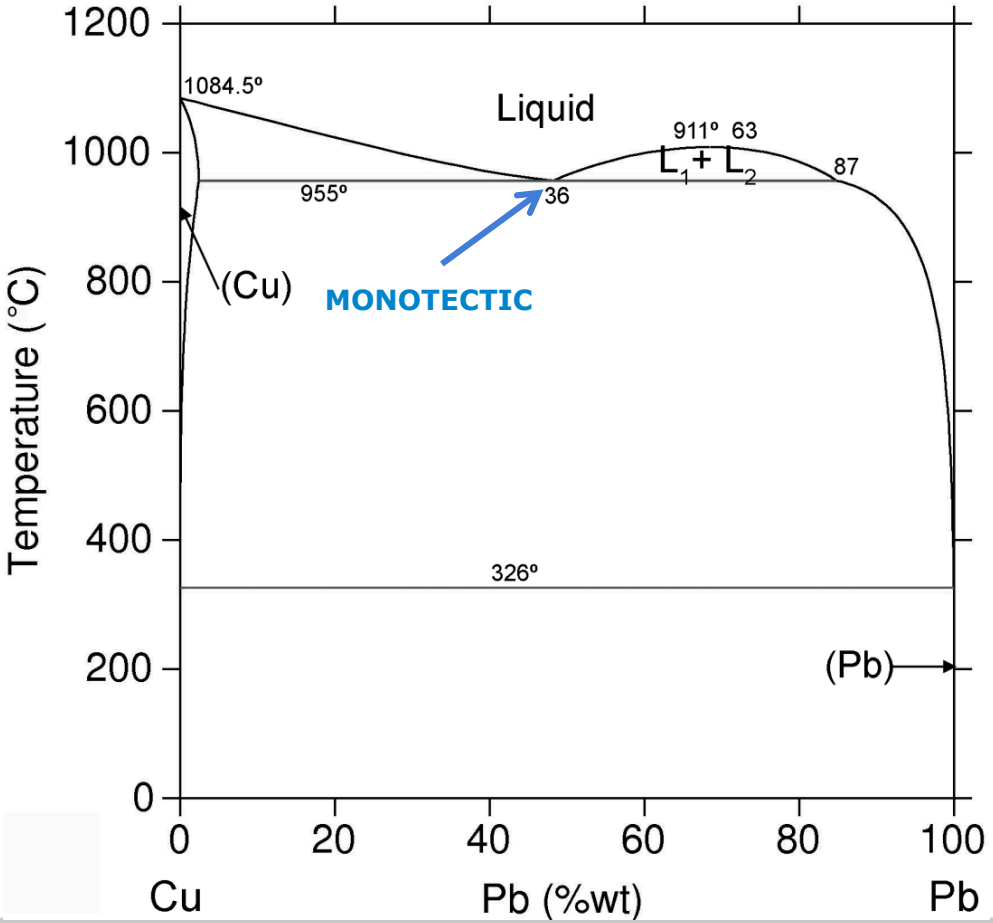
Mototectic reaction:

$$L_1 \rightarrow L_2 + \alpha$$

It occurs when there is a miscibility gap in the liquid phase:

Miscibility gap: two liquid phases co-exist

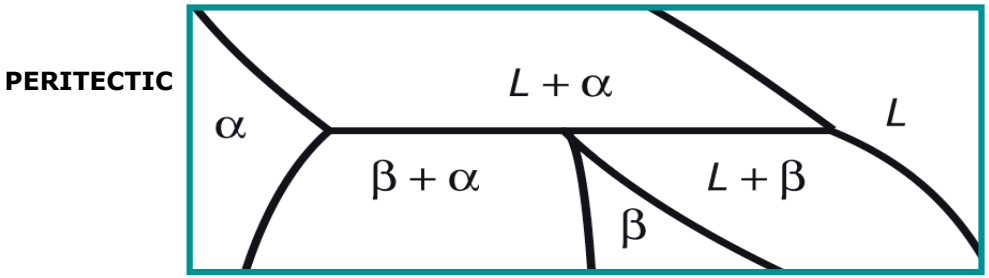


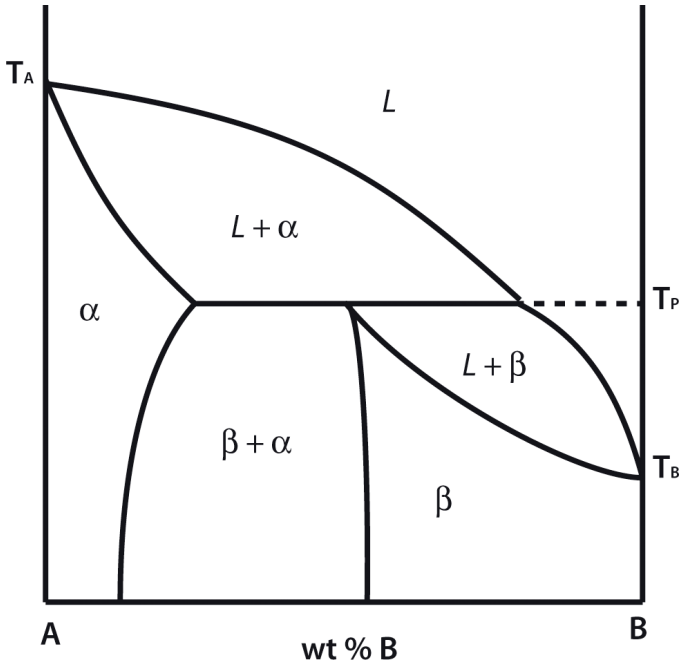


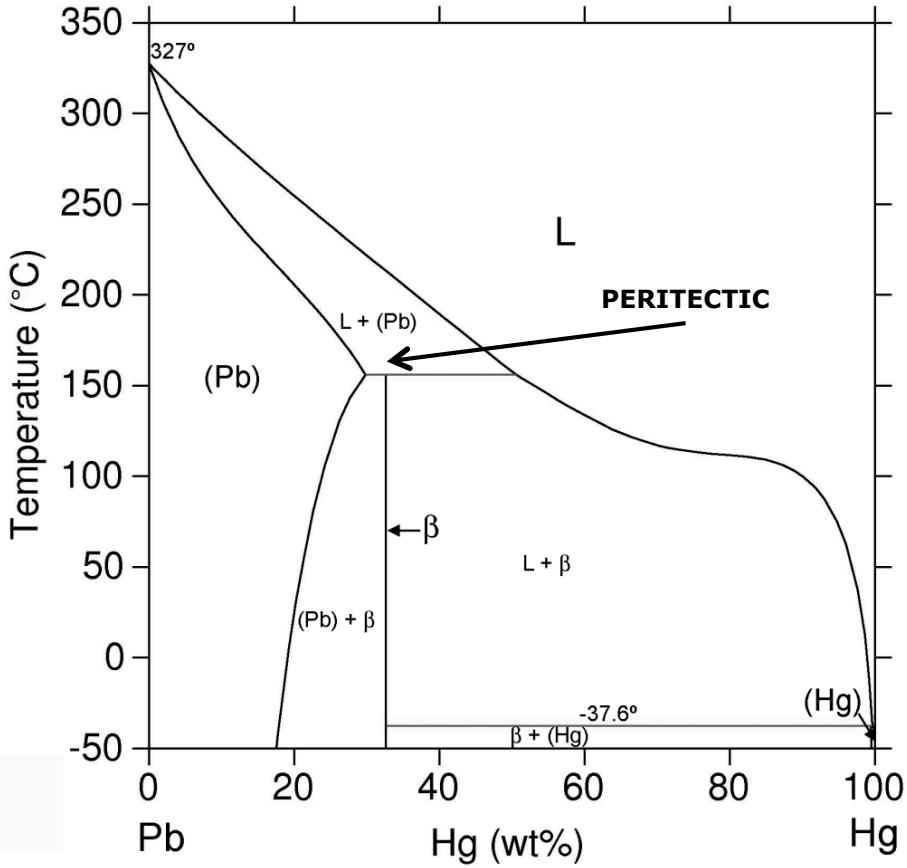
INVARIANT REACTIONS

Peritectic reaction:

$$\alpha + L \rightarrow \beta$$





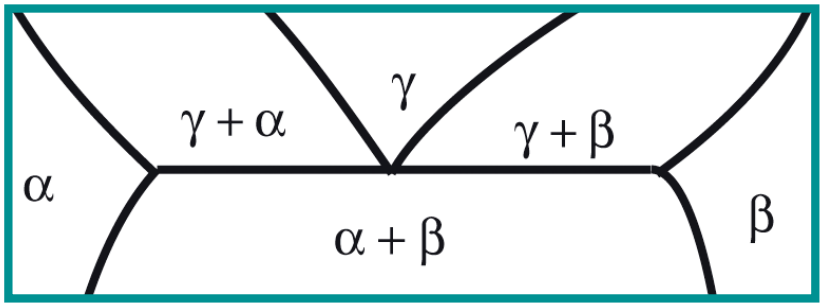


INVARIANT REACTIONS

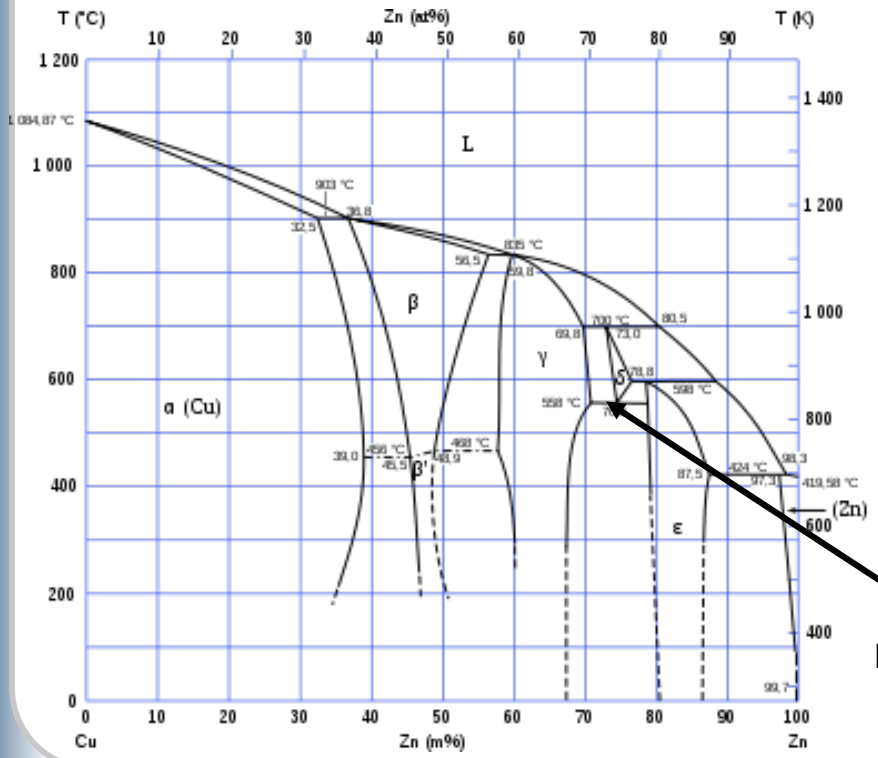
Eutoctoid reaction:

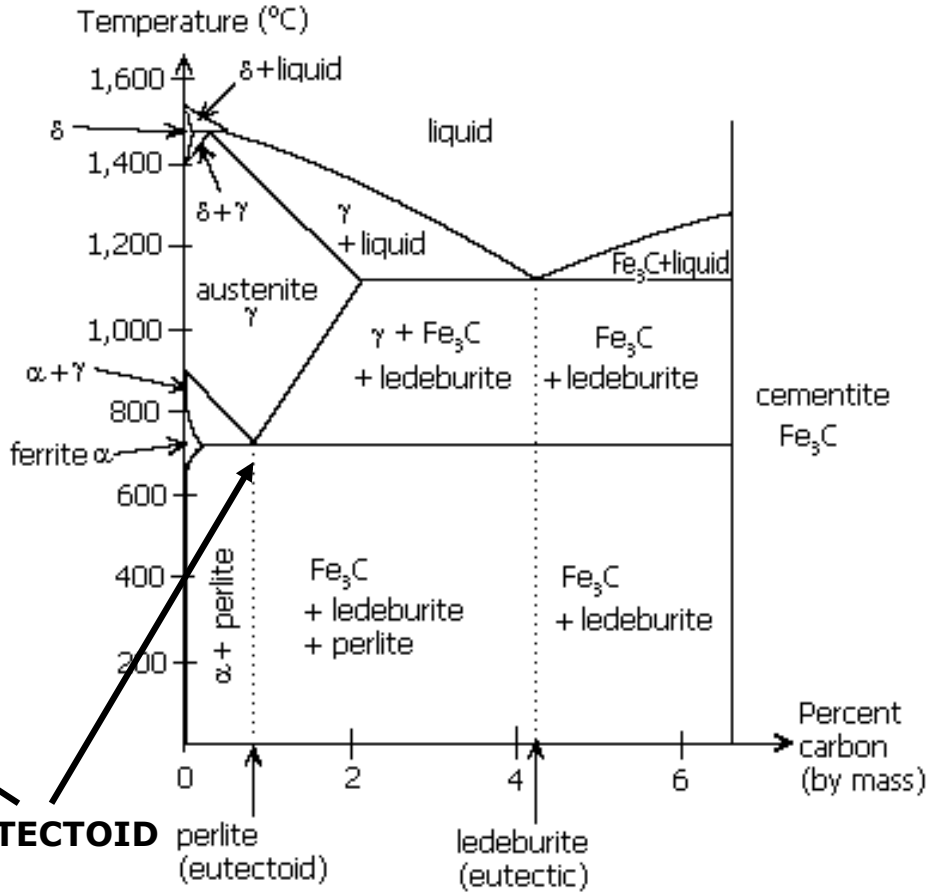
$$\gamma \rightarrow \alpha + \beta$$

EUTECTOID



Eutoctoid and Peritectoid reactions:
Solid state reactions





EUTECTOID

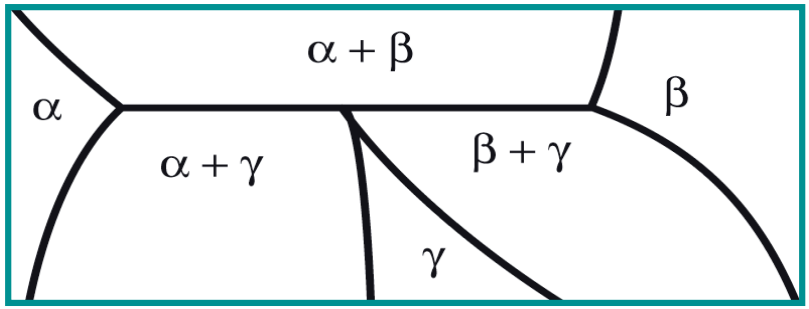
http://commons.wikimedia.org/wiki/File:Phase_diag_iron_carbon.PNG

INVARIANT REACTIONS

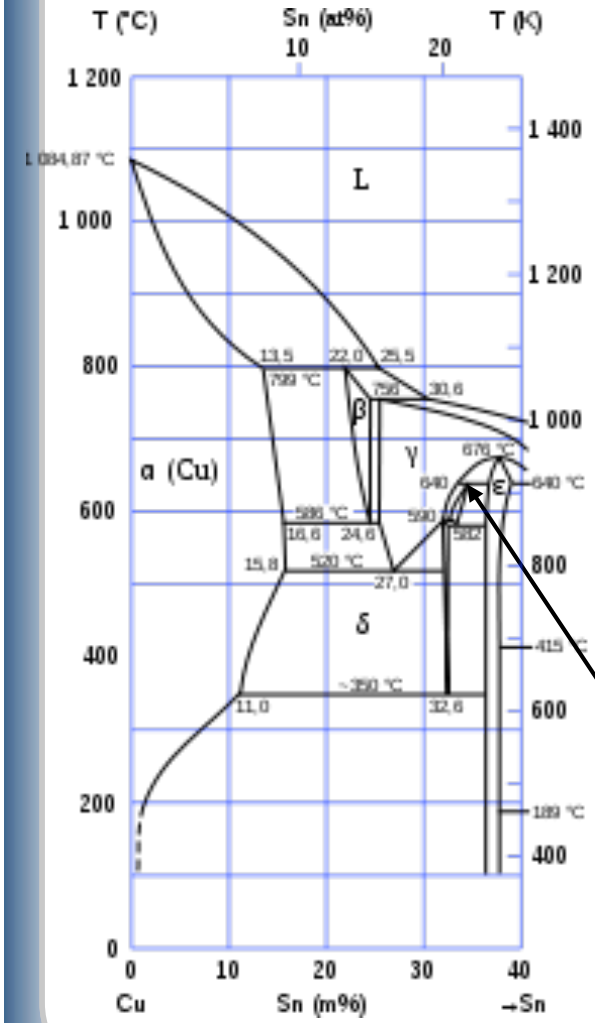
Peritectiod reaction:

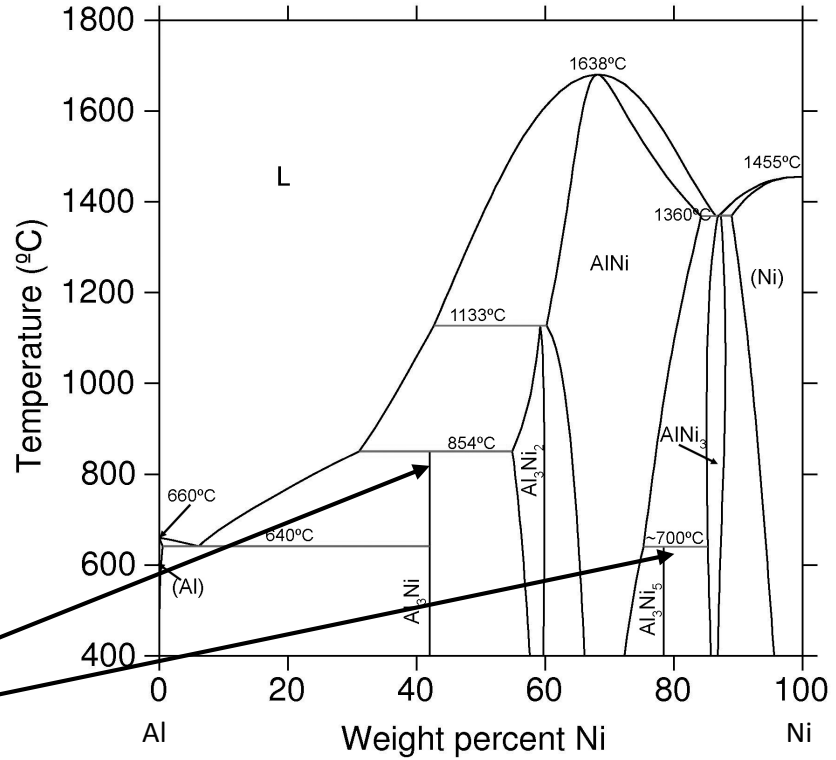
$$\beta + \alpha \rightarrow \gamma$$

PERITECTOID



Two solid phases react to give a completely different solid phase





PERITECTOID

INTERMETALLICS

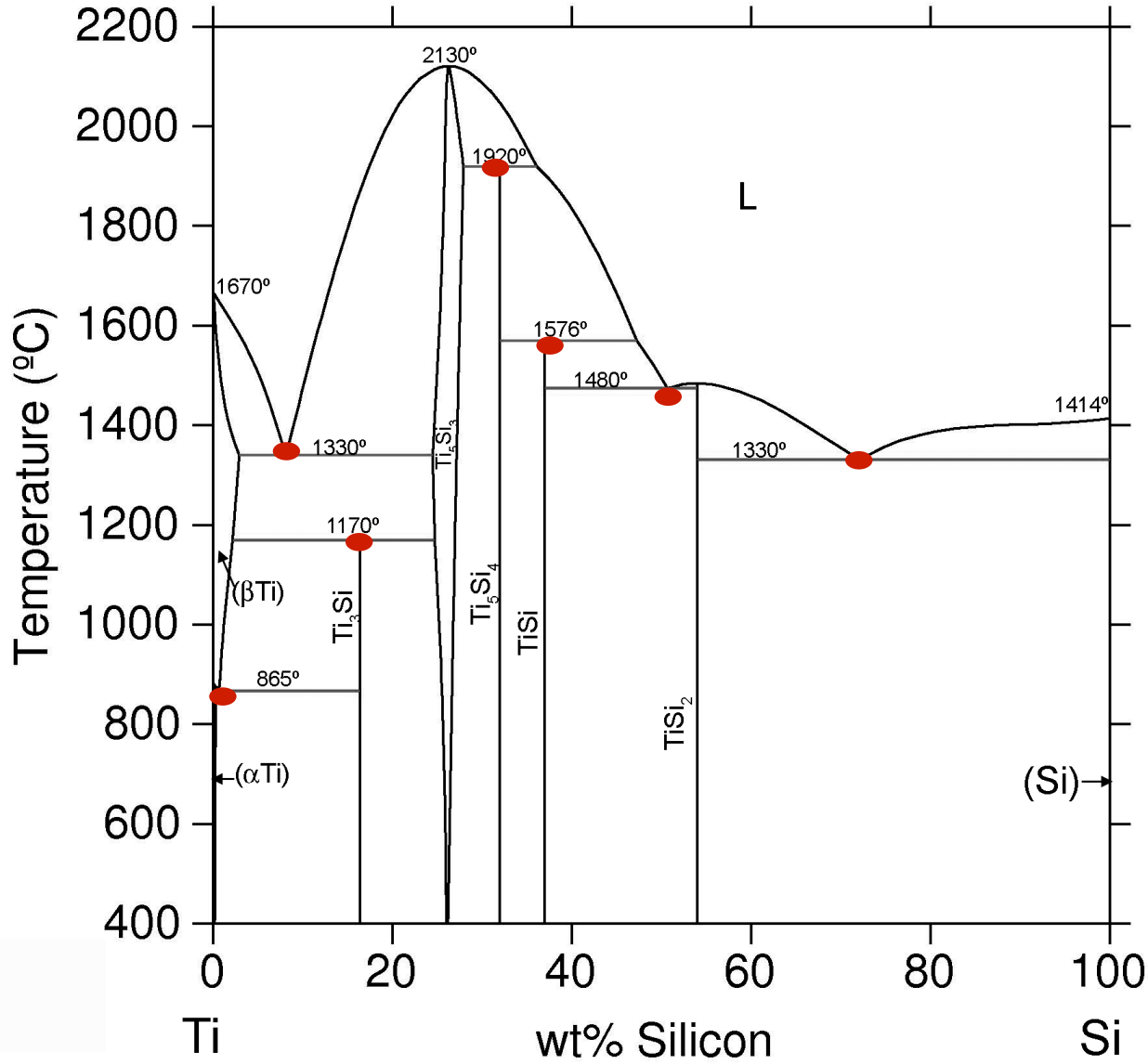
- Intermetallic compound (or intermediate solid solution) : made up of two or more components, producing a new phase with its own composition, crystal structure and properties

CONGRUENT AND INCONGRUENT MELTING

- A component is said to ***melt congruently*** when the liquid formed upon melting has the same composition as the solid from which it was formed
  - e.g. pure metals

- A component is said to ***melt incongruently*** when the liquid formed upon melting has a composition other than the one of the solid from which it was formed
  - e.g. peritectic reaction: $\alpha + L \rightarrow \beta$ ..

INTERMETALLICS. CONGRUENT AND INCONGRUENT MELTING



Congruent melting:
Ti_5Si_3 ; $TiSi_2$

Incongruent melting:
Ti_3Si ; Ti_5Si_4; TiSi