Phase Diagrams

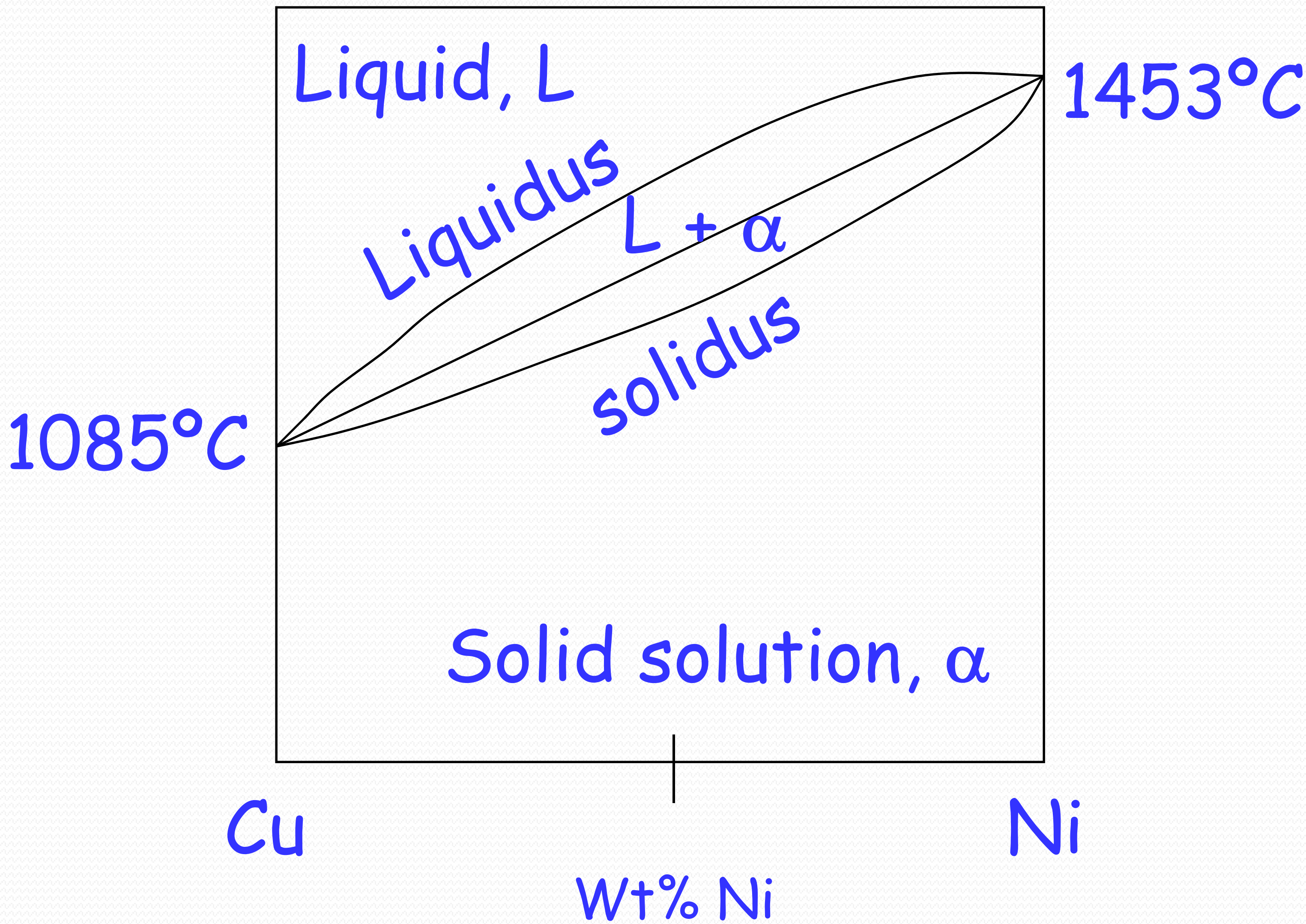
Why do cocktail ice served in expensive restaurants are clear whereas the ice formed in your refrigerator is cloudy?

What is a solder alloy?

What is the best composition for solder?

How is ultrpure Si for computer chips produced?

Melting point of an alloy



Equilibrium phase diagram

or

Equilibrium diagram

or

Phase diagram

A diagram in the space of relevant thermodynamic variables (e.g., T and x) indicating phases in equilibrium is called a phase diagram.

Components

The independent chemical species (element or compound) in terms of which the composition of the system is described are called components.

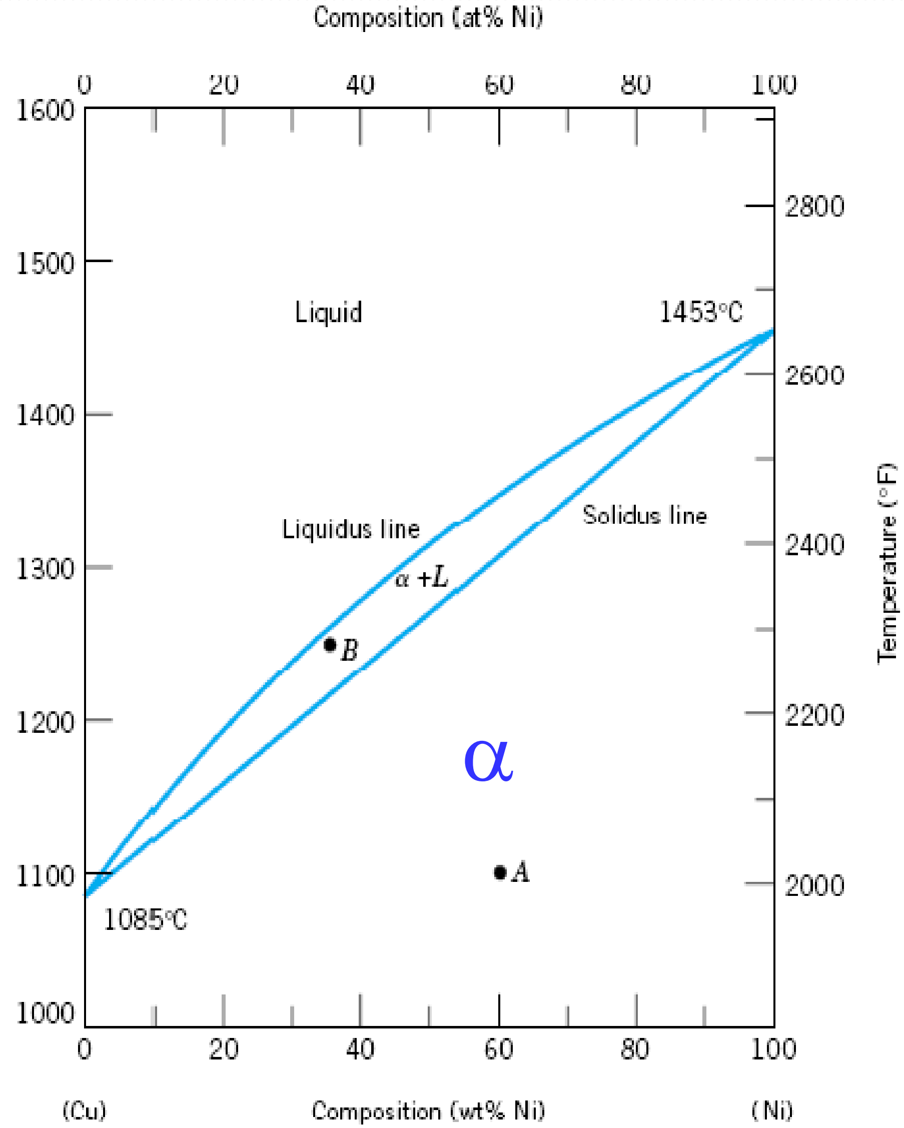
System	components	phases
Water	H_2O	liquid
Water +ice	H_2O	Liquid+solid
shikanji	nimbu, chini and pani	liquid solution
Mild steel	Fe + C	$\alpha + Fe_3C$

A single component phase diagram:
Unary diagram

A two-component phase diagram:
Binary diagram

A three-component phase diagram:
Ternary diagram

Cu-Ni binary phase diagram



Any given point (x,T) on the phase diagram represents an alloy of composition x held at equilibrium at temperature T

Point A:
60 wt% Ni at 1100°C

Point B:
35 wt% Ni at 1250°C

Callister, Fig. 9.2

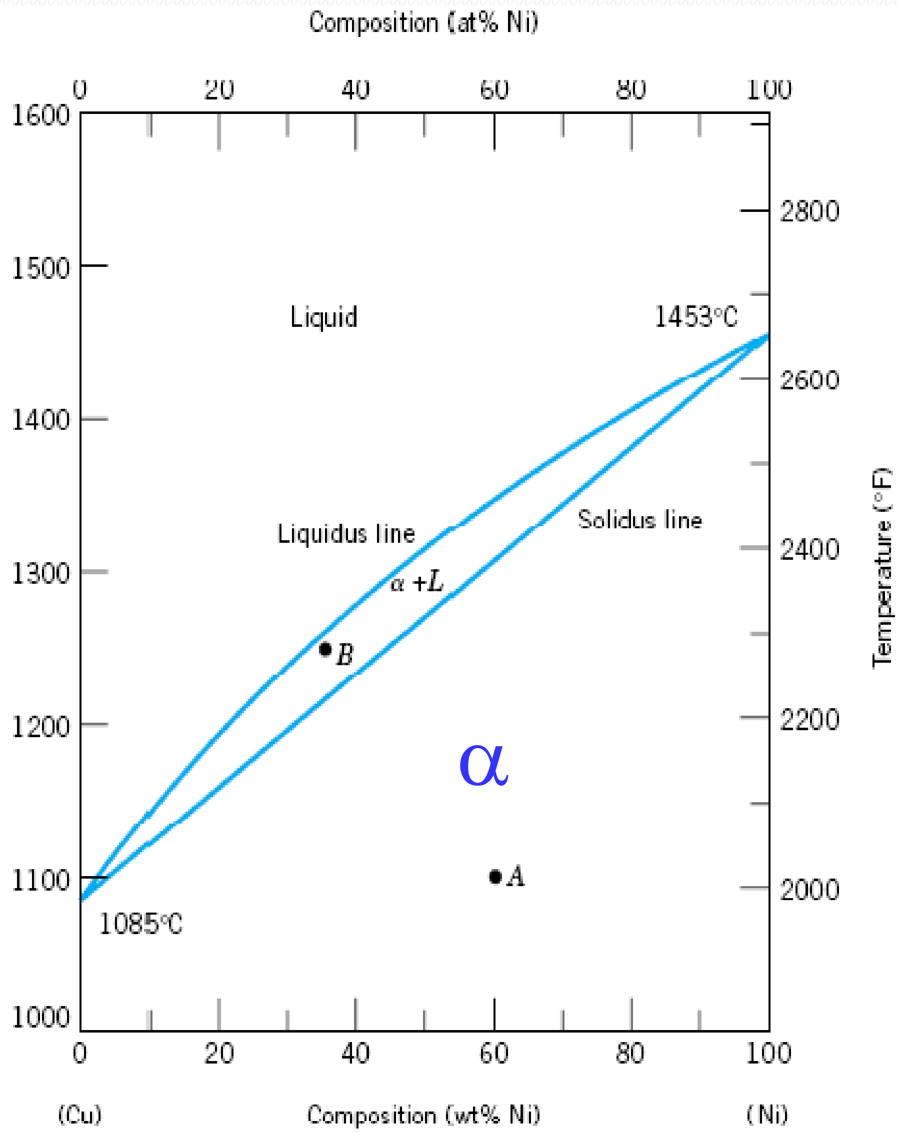
Phase Diagrams

For any given point (x,T) the phase diagram can answer the following:

1. What phases are present?
2. What are the phase compositions?
3. What are the relative amounts of the phases (phase proportions or phase fractions)?

Point A:

60 wt% Ni at 1100°C



Q: Phase present?

Ans: α

Q: Phase composition ?

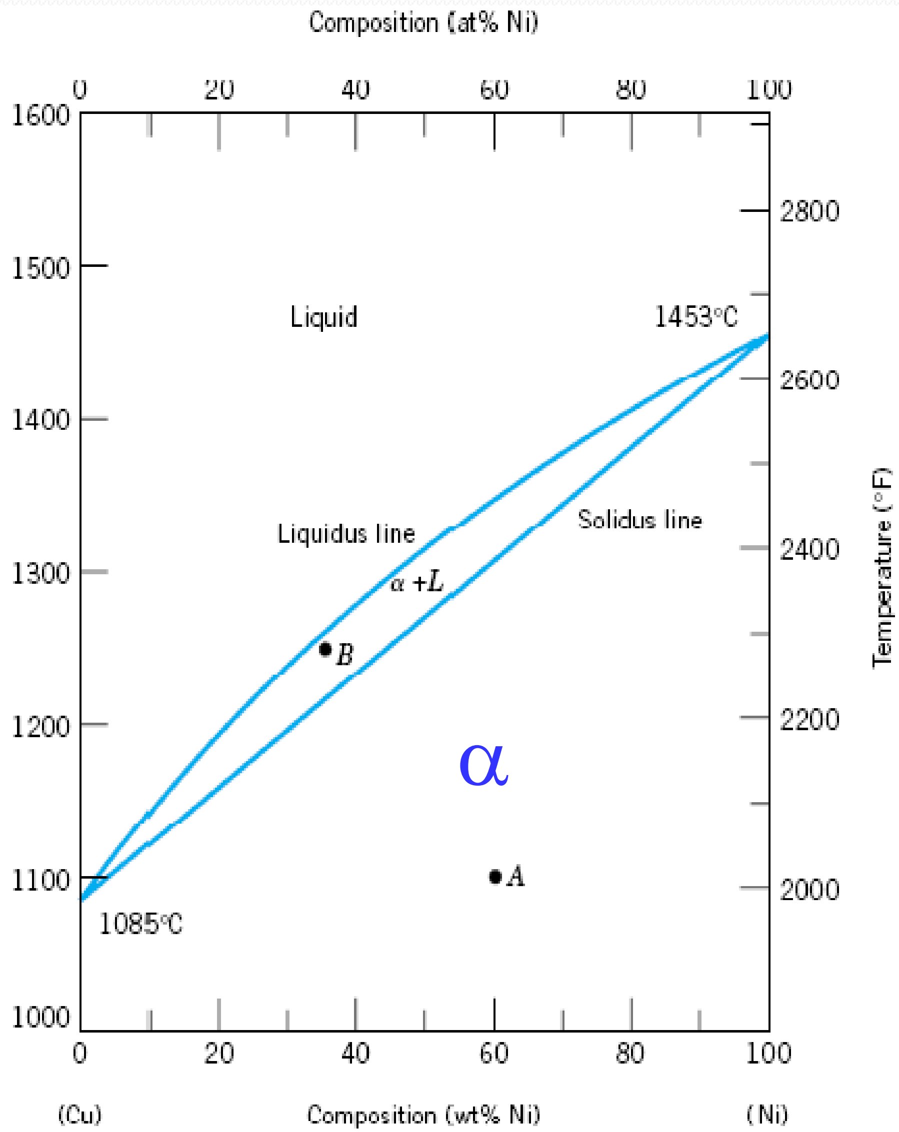
Ans: 60 wt%Ni

Q: Phase amount ?

Ans: 100%

Point B:

35 wt% Ni at 1250°C



Q: Phases present?

Ans: α + L

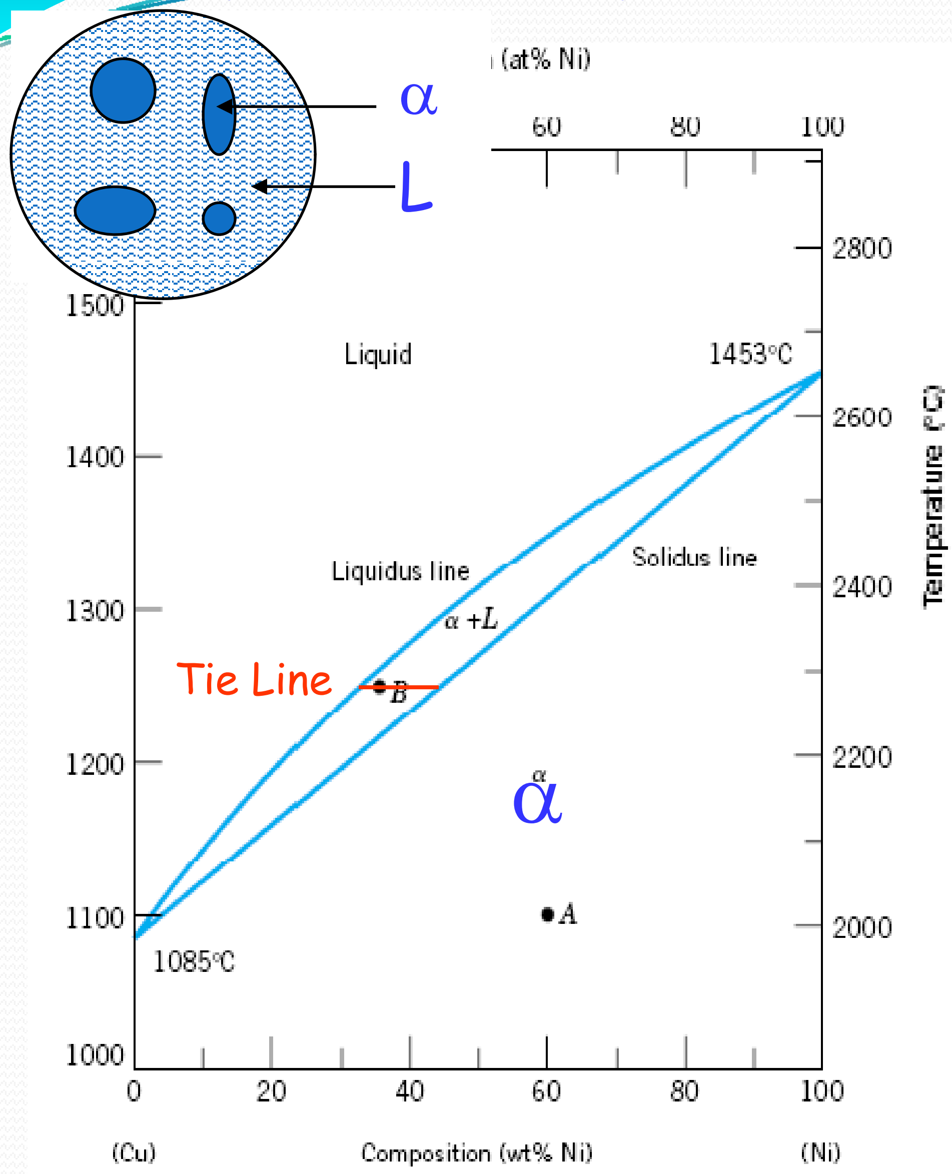
Q: Phase compositions ?

Tie Line Rule

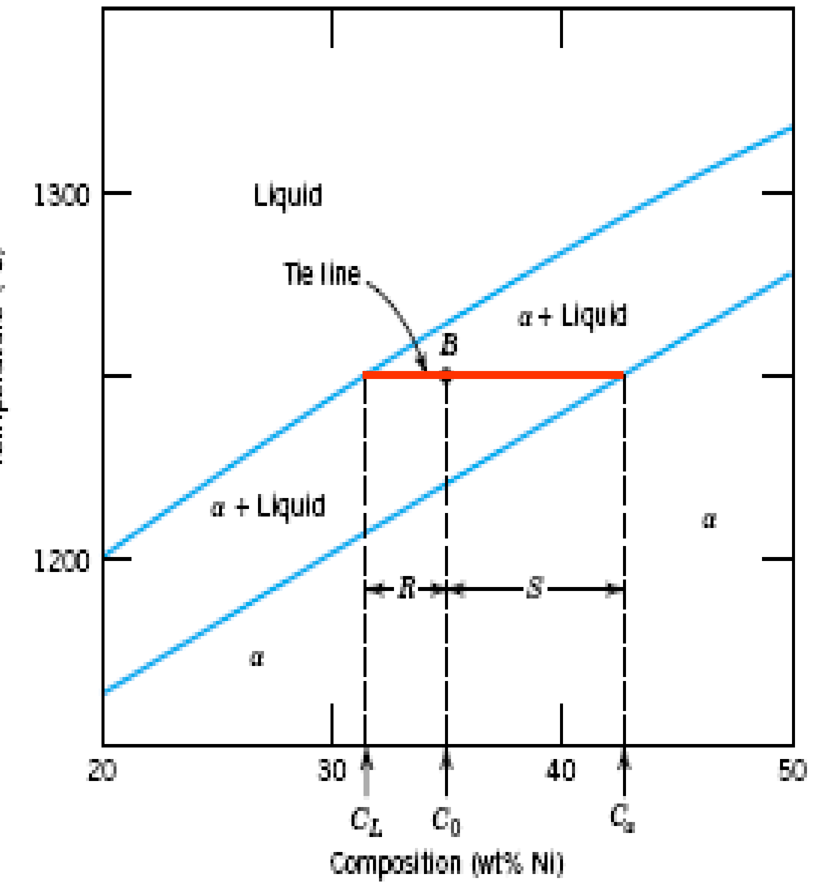
Q: Phase amounts ?

Lever Rule

Composition of phases in the two-phase region



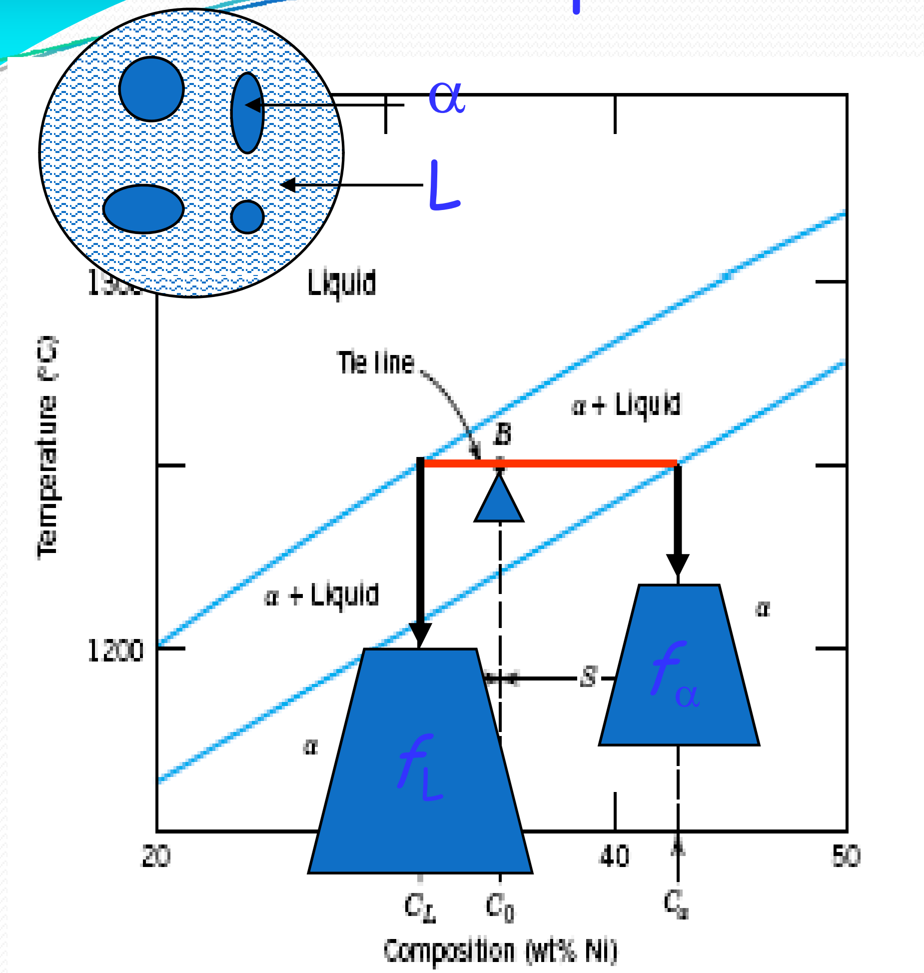
Tie Line Rule



C_L = 31.5 wt% Ni

C_α = 42.5 wt% Ni

Amount of phases in the two-phase region



Tie-Line: A lever

Alloy composition C_0: Fulcrum

f_L: weight at liquidus point

f_α: weight at solidus point

The lever is balanced

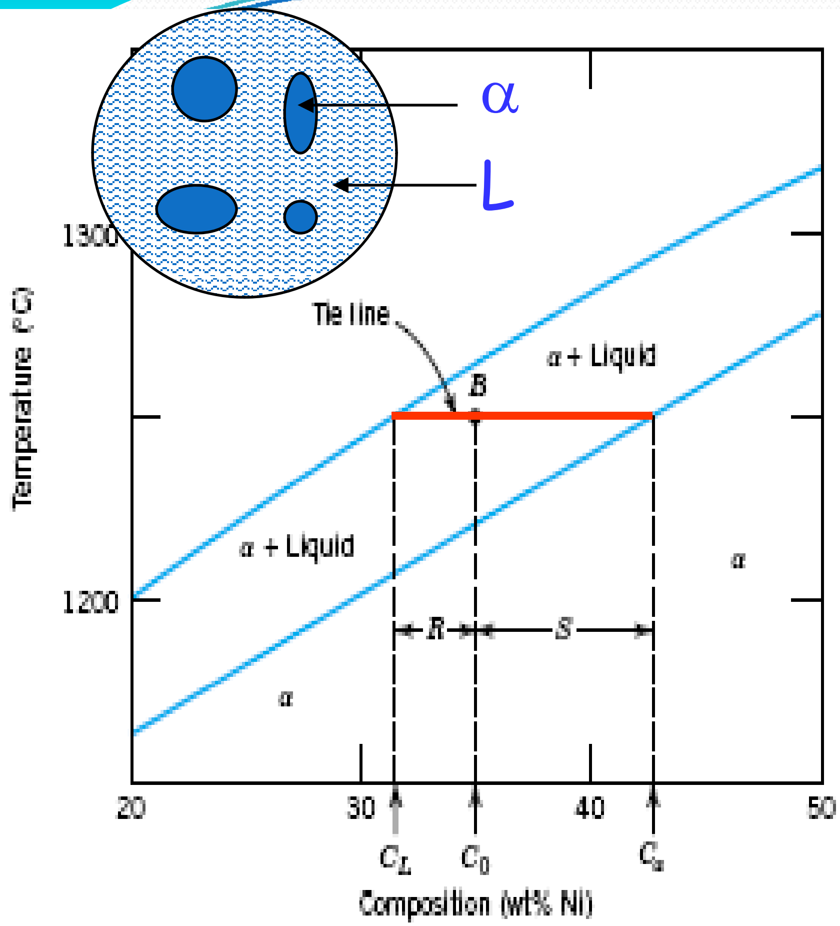
$$f_L(C_0 - C_L) = f_\alpha(C_\alpha - C_0)$$

$$f_L + f_\alpha = 1$$

Tie Lever Rule

$$f_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{opposite\ \ lever\ \ arm}{total\ \ lever\ \ arm}$$

The Lever Rule: A Mass balance Proof   Prob. 7.6



Wt of alloy = W

Wt of α in alloy = $f_\alpha W$

Wt of L in alloy = $f_L W$

Wt of Ni in alloy = $W\, C_0/100$

Wt of Ni in α = $f_\alpha W C_\alpha/100$

Wt of Ni in L = $f_L\, W C_L/100$

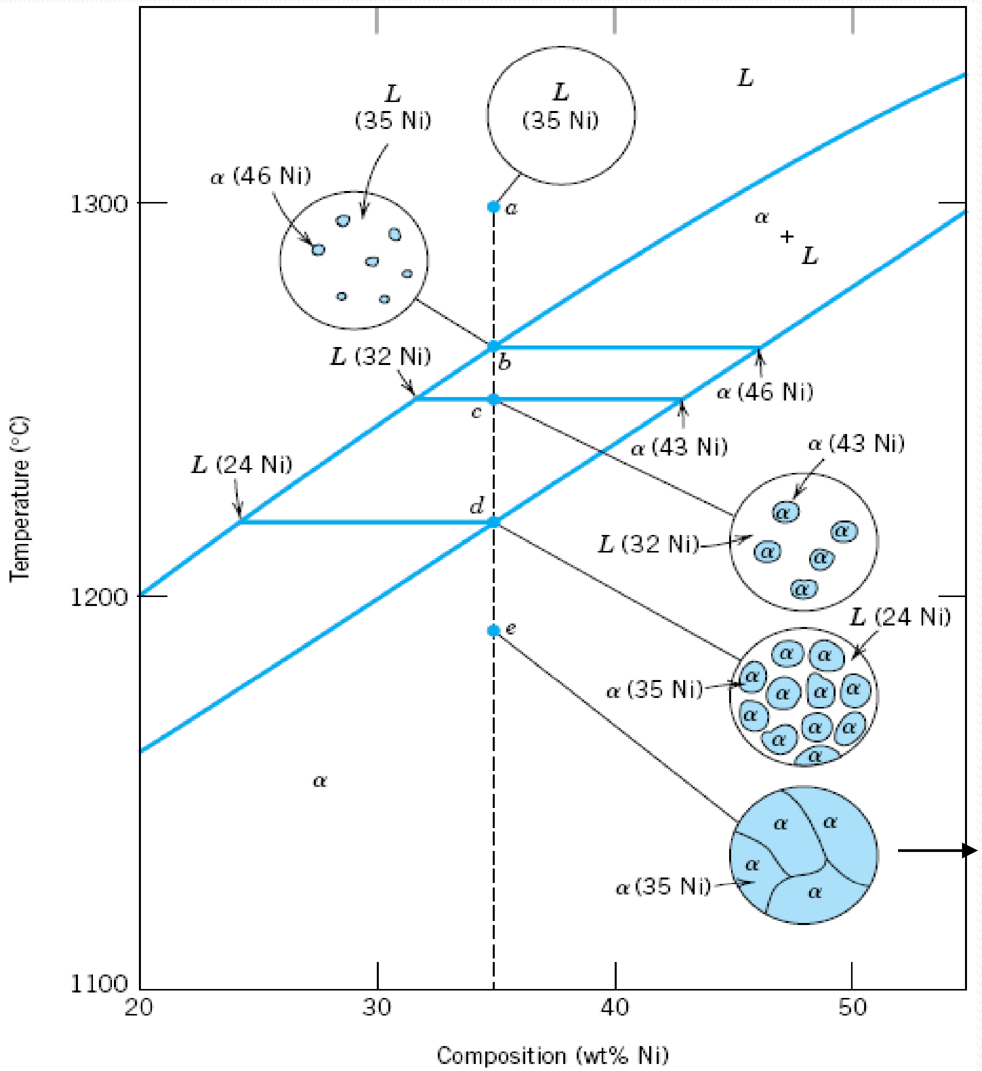
Wt of Ni in alloy = Wt of Ni in α + Wt of Ni in L

$$C_\alpha f_\alpha + C_L f_L = C_0$$

$$f_\alpha + f_L = 1$$

$$f_L = \frac{C_\alpha - C_0}{C_\alpha - C_L} = \frac{opposite\ \ lever\ \ arm}{total\ \ lever\ \ arm}$$

Development of Microstructure during solidification



$$f_\alpha = \frac{35-32}{43-32} = \frac{3}{11} = 0.273$$

$$f_L = 1 - f_\alpha = 0.727$$

Single phase polycrystalline α

Solder alloy?

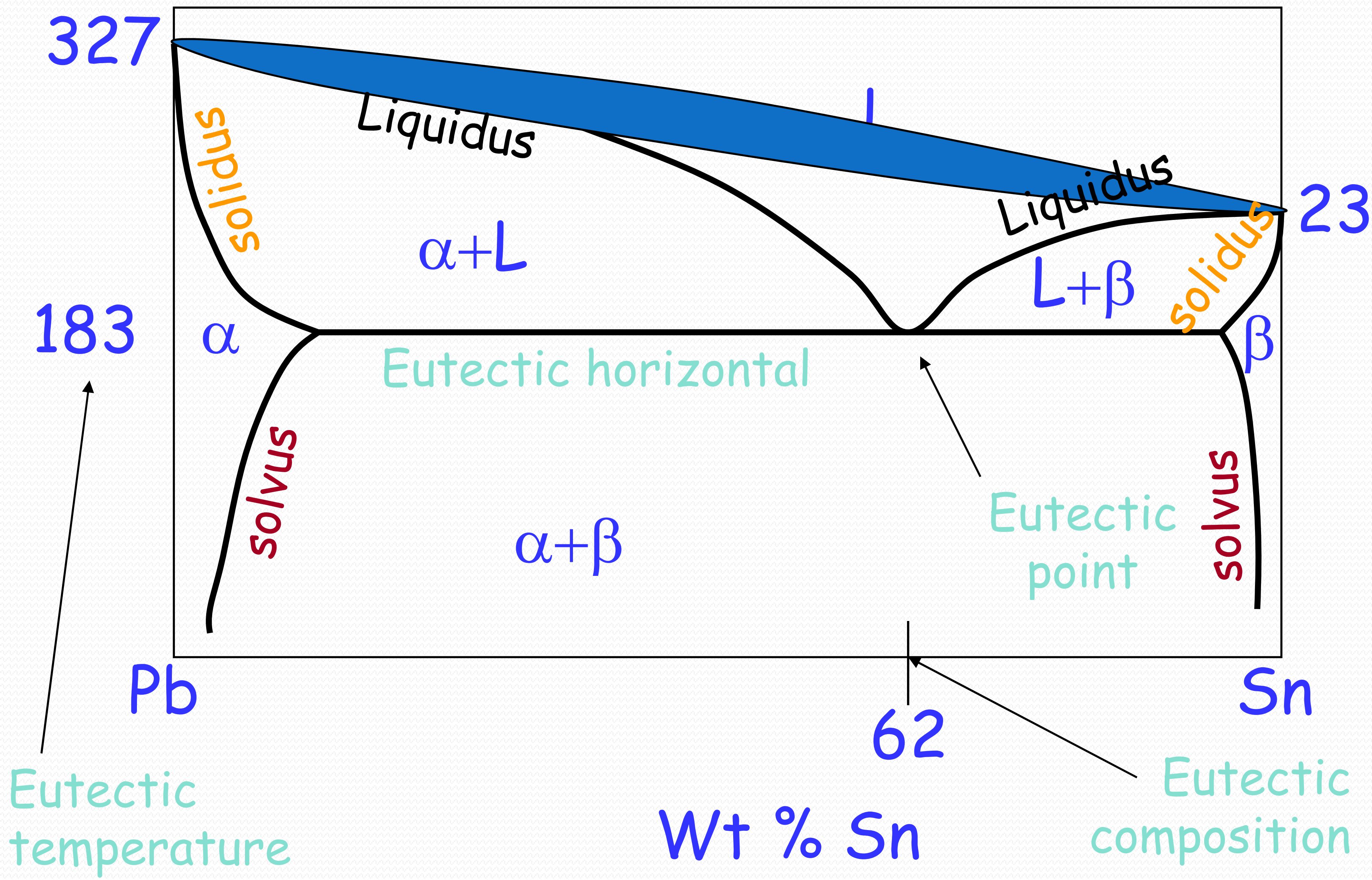
An alloy of Pb and Sn

What is best composition of the solder alloy?

Requirements:

1. should melt easily
2. should give a strong joint

Solder alloy 1-2-1 rule Eutectic diagram



Pb: monatomic fcc

Sn: monatomic bct

α: Pb rich substitutional solid solution of Pb and Sn

crystal structure: monatomic FCC

β: Sn rich substitutional solid solution of Pb and Sn

crystal structure: monatomic BCT

Woods metal tea party

Bi 50.0 wt%
Pb 25.0 wt%
Cd 12.5 wt%
Sn 12.5 wt%

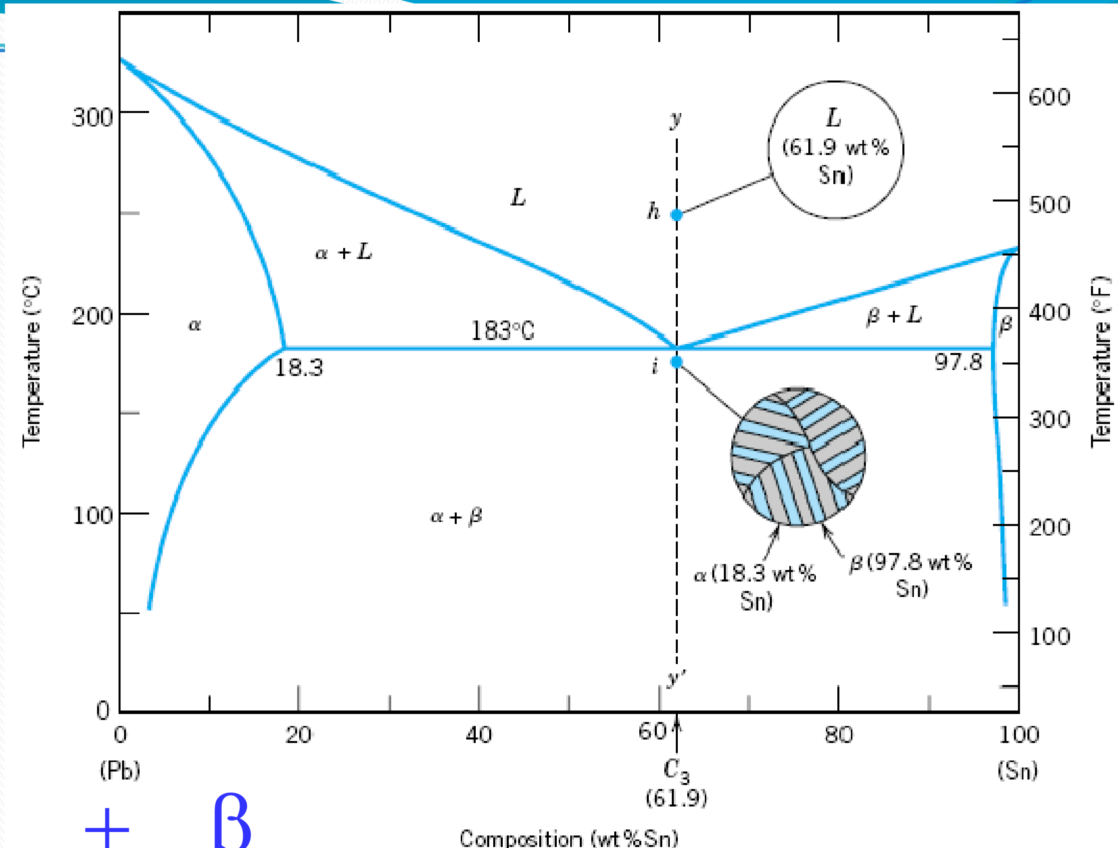
An eutectic alloy with m.p. of 70°C

100 g US$ 181

Anti-Fire Sprinklers

Eutectic reaction

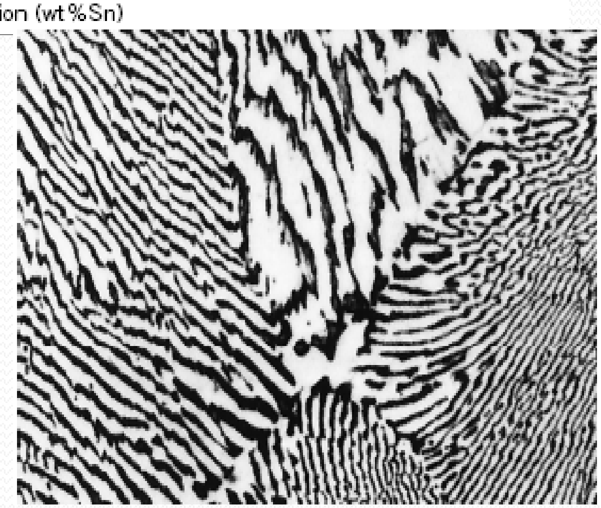
Invariant reaction



$$L \xrightarrow[183°C]{cool} \alpha + \beta$$

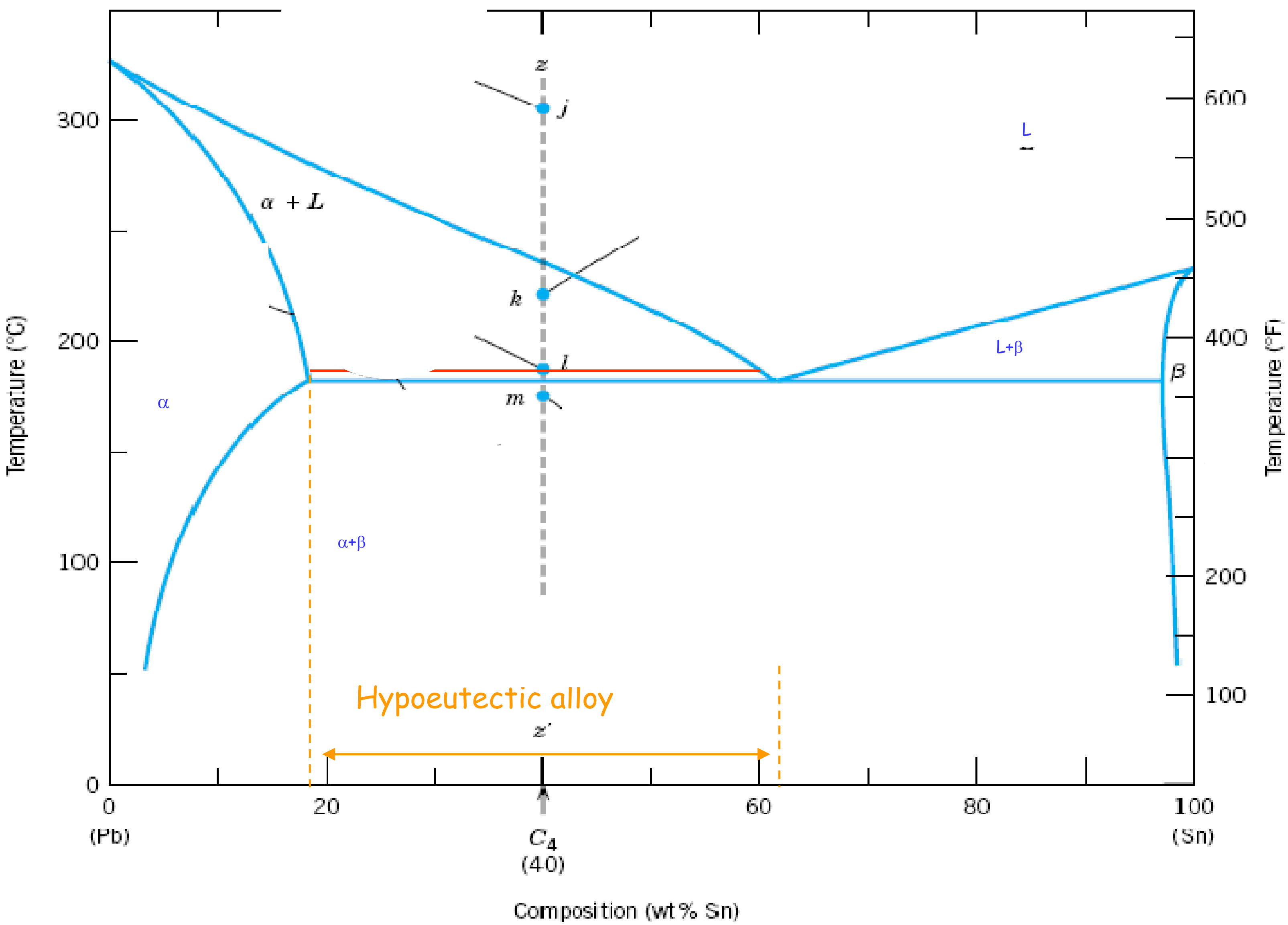
L		α	β
62 wt%Sn		18 wt%Sn	97 wt%Sn

(α + β: Eutectic mixture)



375 X

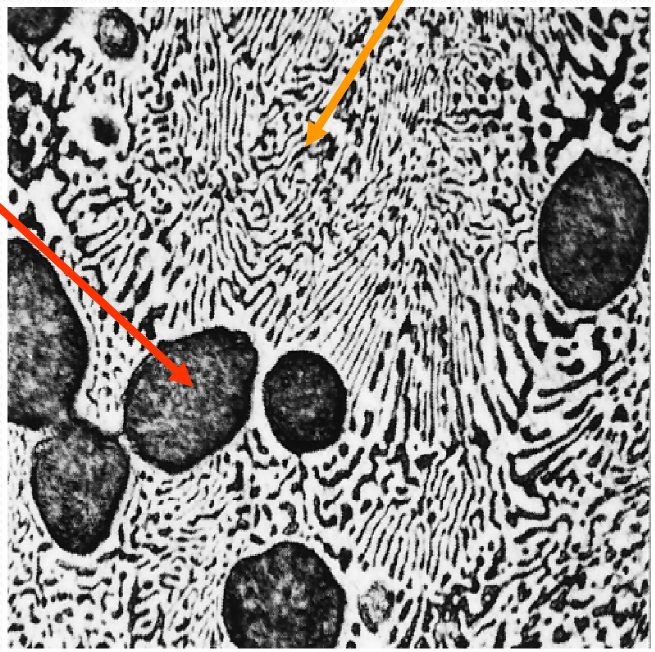
Callister Figs. 9.11, 12

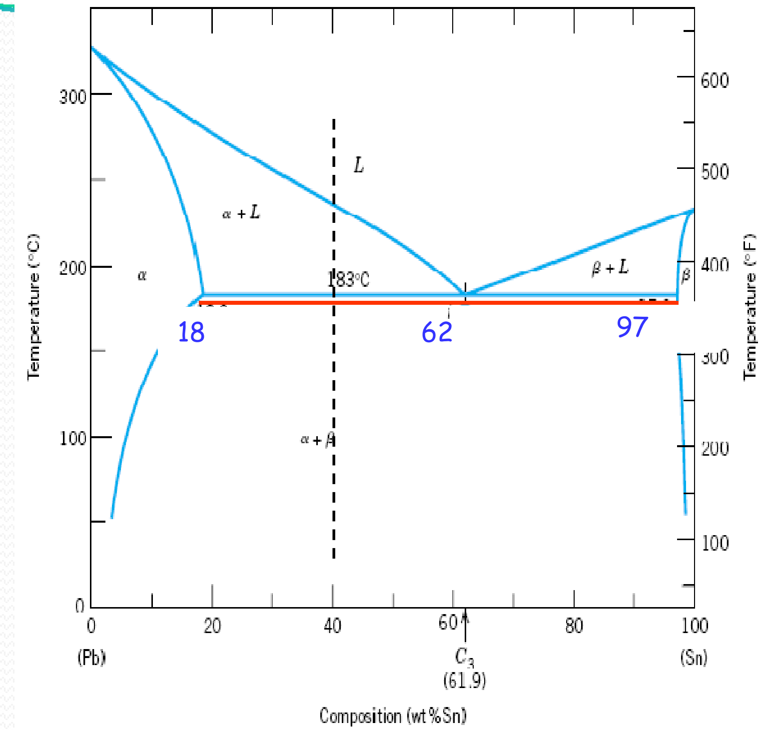


Microstructure of hypoeutectic alloy

Eutectc mixture $\alpha+\beta$

Proeutectic or Primary α

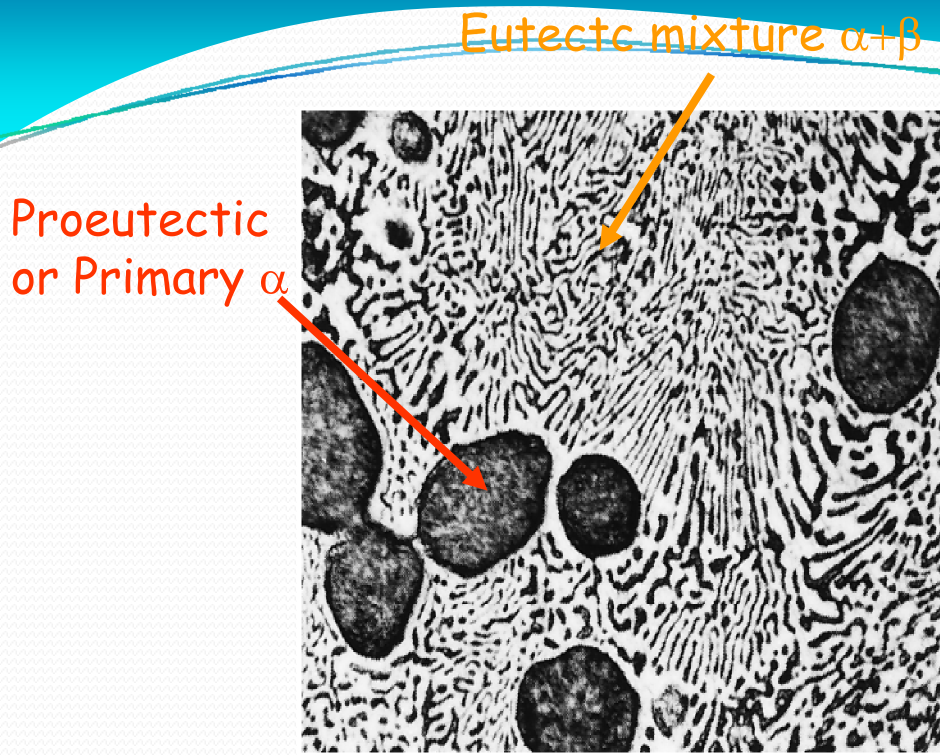


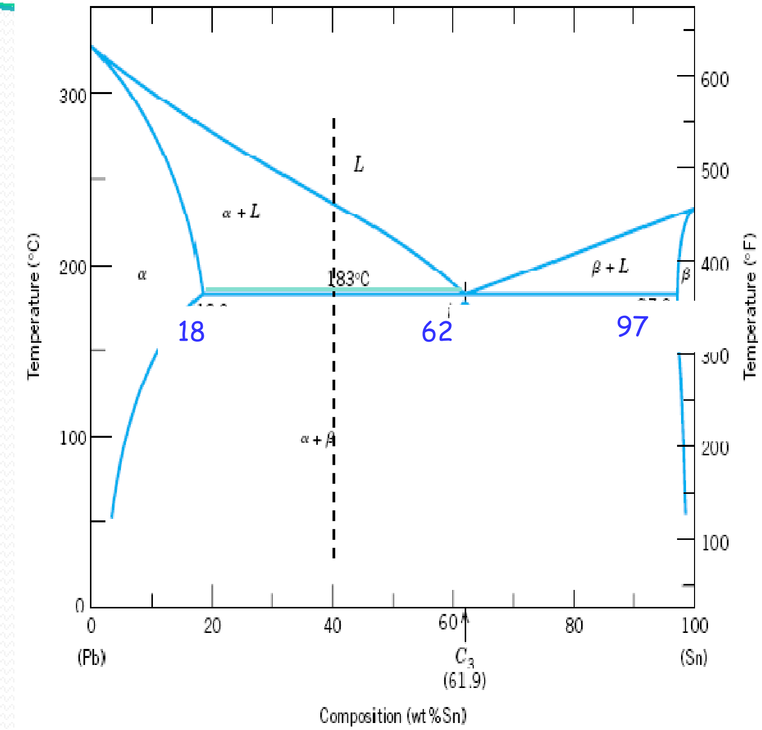


Amount of total α and total β at a temperature just below 183°C

Tie line just below 183°C (red)

$$f_{total\ \alpha} = \frac{97 - 40}{97 - 18} = \frac{57}{79} = 0.72$$





Amount of proeutectic α at a temperature just below 183°C

= Amount of α at a temperature just above 183°C

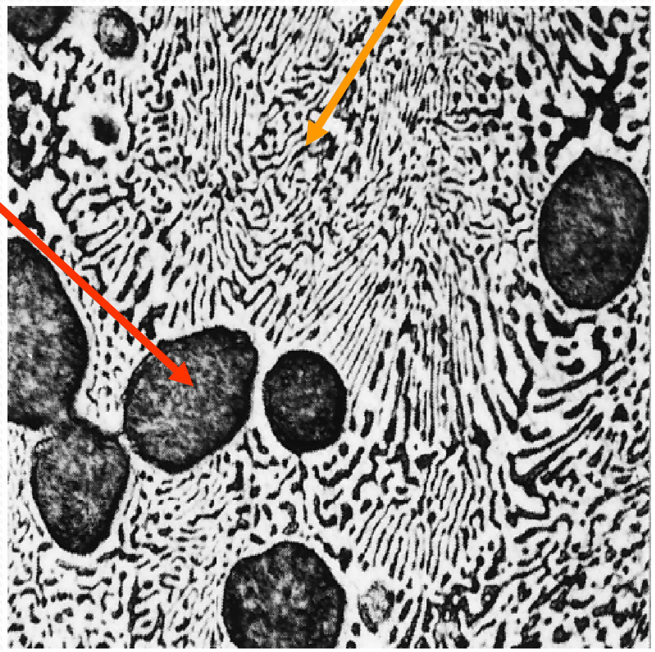
Tie line just above 183°C (green)

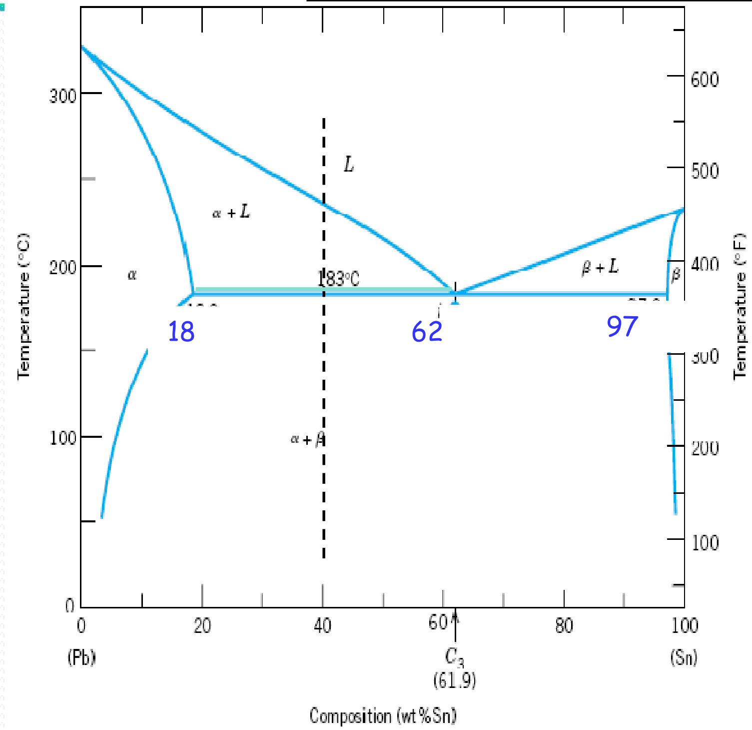
$$f_{pro\ \alpha} = \frac{62 - 40}{62 - 18} = \frac{22}{44} = 0.5$$

EXPERIMENT 5

Eutectc mixture α+β

Proeutectic or Primary α





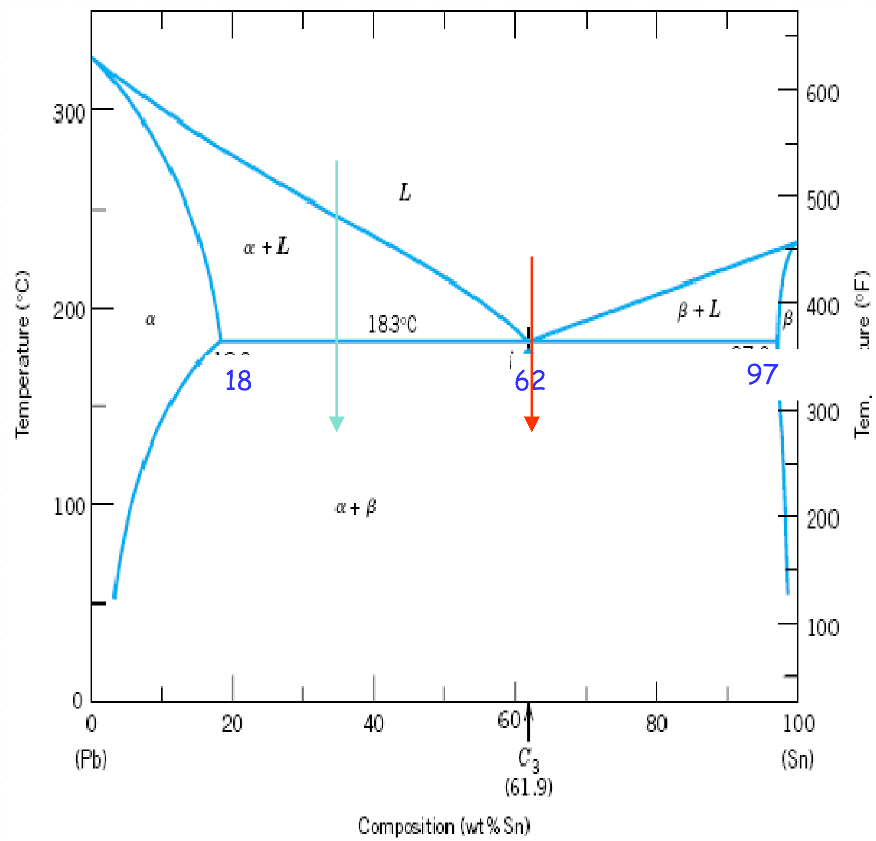
Let the fraction of proeutectic α in micrograph $f_{pro\ \alpha}$= 0.25

Let the composition (wt% Sn) of the alloy be C_0

Tie line just above 183°C (green)

$$f_{pro\ \alpha} = \frac{62 - C_0}{62 - 18} = 0.25$$

Optimum composition for solders



For electronic application

Eutectic solder
62 wt% Sn

Minimum heating

For general application

Hypoeutectic solder

Cheaper

Allows adjustment of joint during solidification in the α+L range

Modern Trend

Lead-free solders

Phase diagrams can help in identification of such solders

Sn-Ag-Cu

Please collect your Minor I answer books from Lab in the afternoon

Those who can, do. Those who can't teach

G.B. Shaw

Gibbs Phase Rule

Thermodynamic variables:

P, T, Phase Compositions

(overall composition is not considered)

If there are C components then C-1 compositions have to be specified for each phase

Therefore total number of composition variables:

$$P\,(C-1)$$

With Pressure and Temperature, total number of variables = $P\,(C-1) + 2$

Gibbs phase rule states that one cannot specify all of the above P (C-1) + 2 variables independently in a system at equilibrium

Degrees of Freedom F:

No. of thermodynamic variables that can be specified independently

Gibbs Phase Rule

F = Degrees of freedom

C = No. of components in the system

P = No. of phases in equlibrium

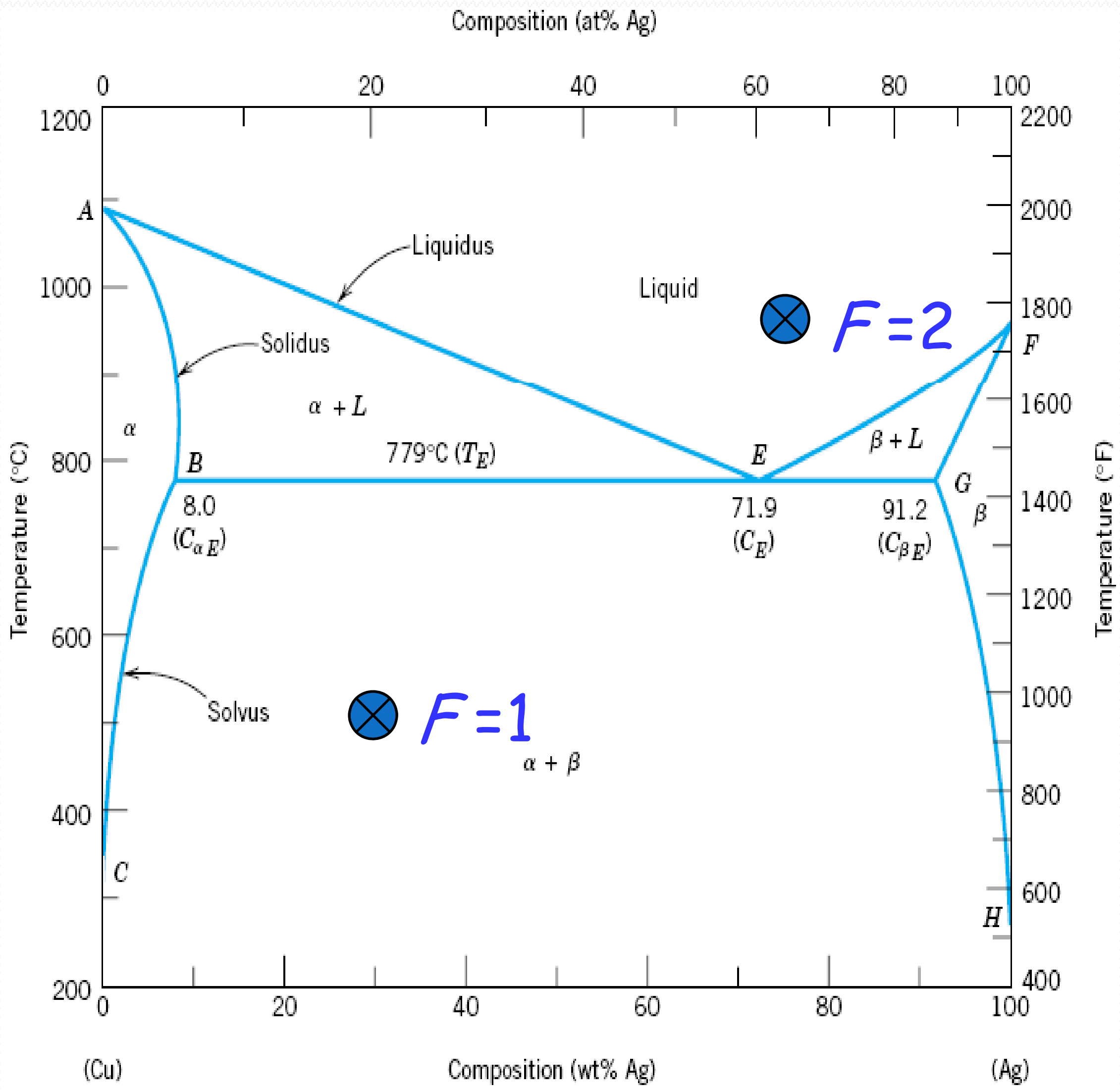
$$F = C - P + 2$$

If pressure and temp both are variables

$$F = C - P + 1$$

If pressure is held constant

$F = C - P + 1$



C=2

F=3-P

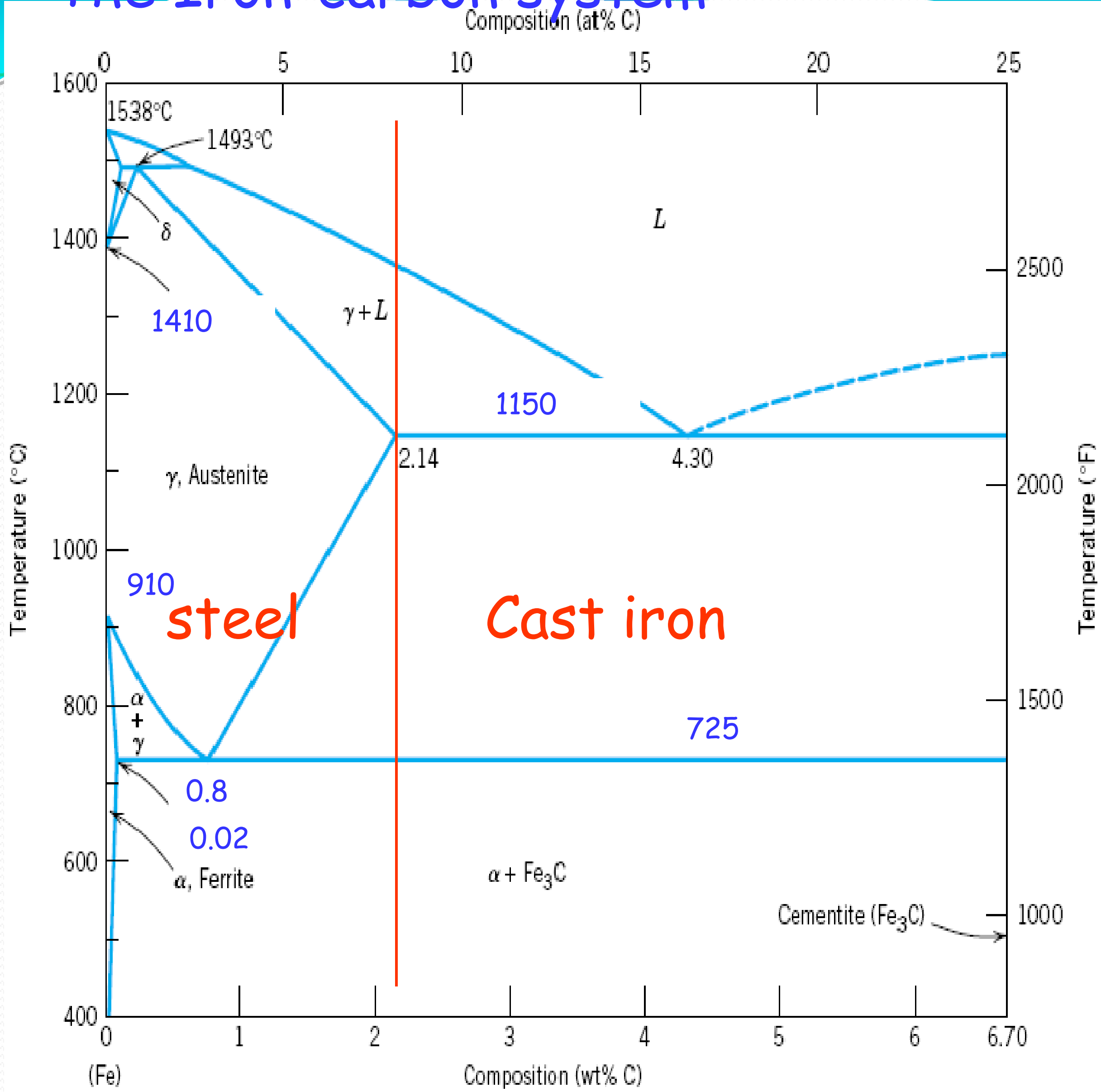
At eutectic reaction P=3

(L, α, β)

F=0

Invariant reaction

The Iron-carbon system



Mild steel
0-0.3 wt% C

Bicycle frame
Ship hull
Car body

Medium C steel
0.4-0.7 wt% C

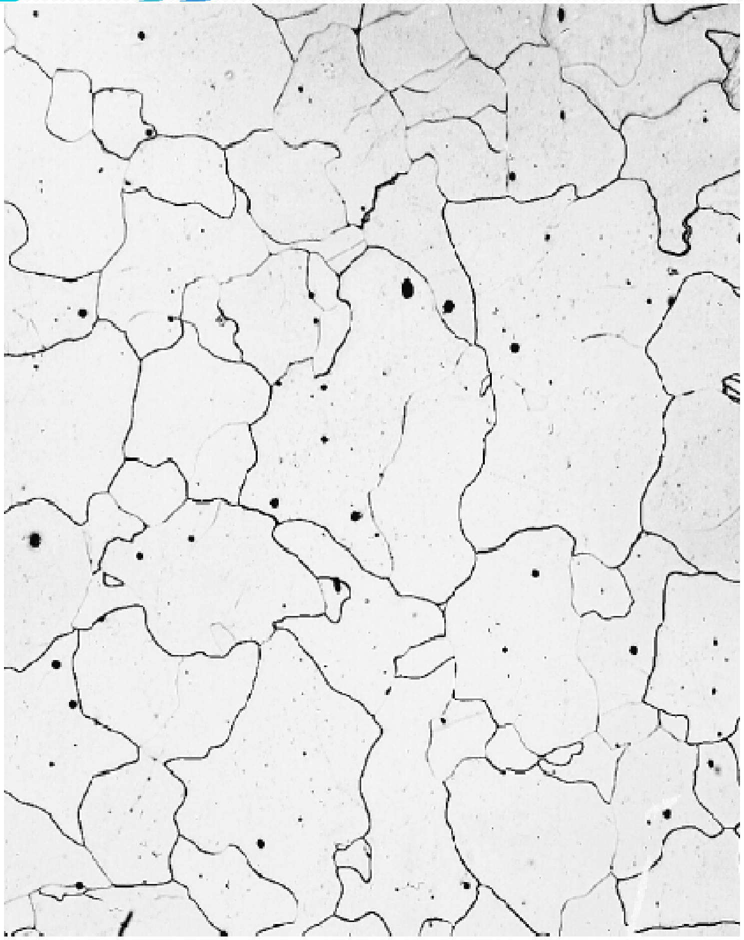
Rail wheel
rail axle
rails

High C steel
0.8-1.4 wt% C

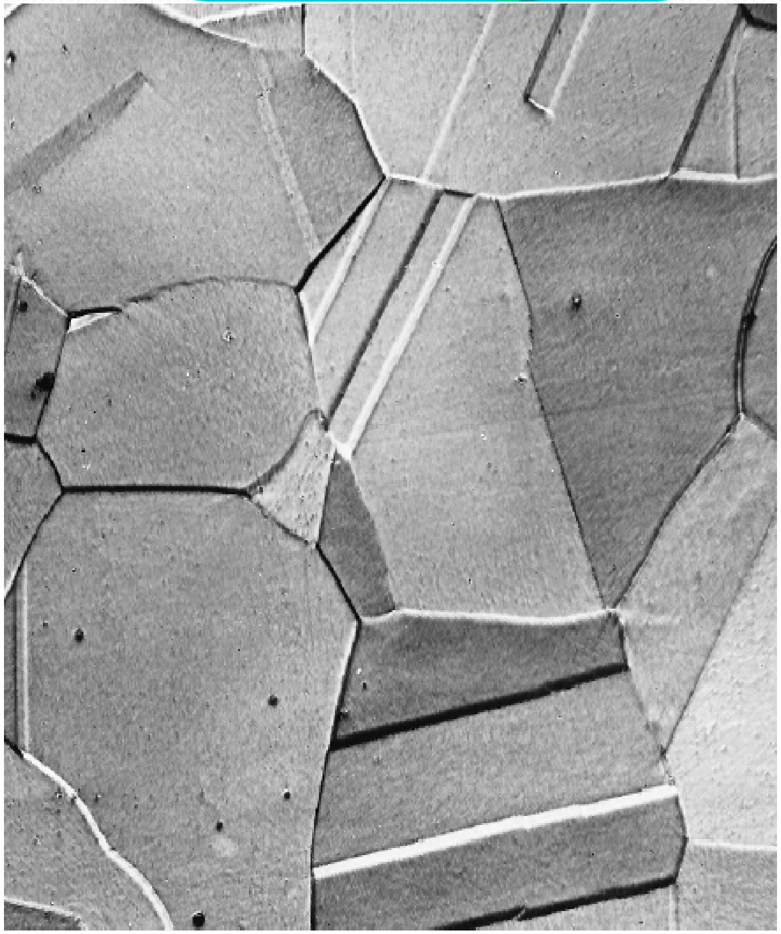
Razor blades
scissors, knives

Phases in Fe-C system

Phase	Symbol	Description
Liquid	L	Liquid solution of Fe and C
δ-Ferrite	δ	Interstitial solid solution of C in δ-Fe (high temperature bcc phase)
Austenite	γ	Interstitial solid solution of C in γ-Fe (FCC phase of Fe)
Ferrite	α	Interstitial solid solution of C in α-Fe (room temperature bcc phase) Soft and Ductile
Cementite	Fe_3C	Intermetallic compound of Fe and C (orthorhombic system) Hard and Brittle



Ferrite



Austenite

Invariant Reactions in Fe-C system

A horizontal line always indicates an invariant reaction in binary phase diagrams

Peritectic Reaction

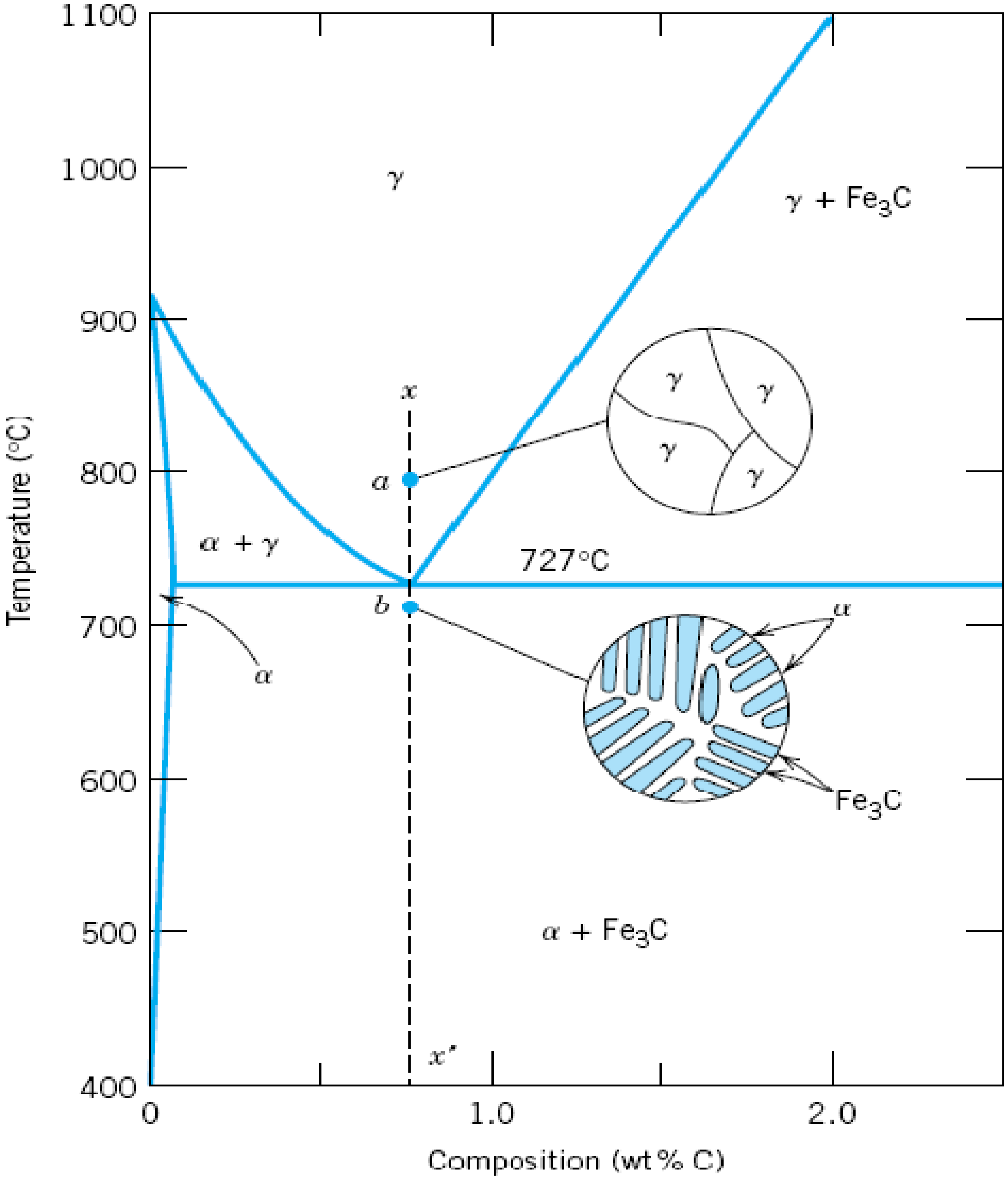
$$\alpha\ (0.1\ wt\%\ C) + L\ (0.5\ wt\%\ C) \xrightarrow{1493^o C} \delta\ (0.18\ wt\%\ C)$$

Eutectic Reaction

$$L\ (4.3\ wt\%\ C) \xrightarrow{1150^o C} \gamma\ (2.1\ wt\%\ C) + Fe_3C\ (6.67\ wt\%\ C)$$

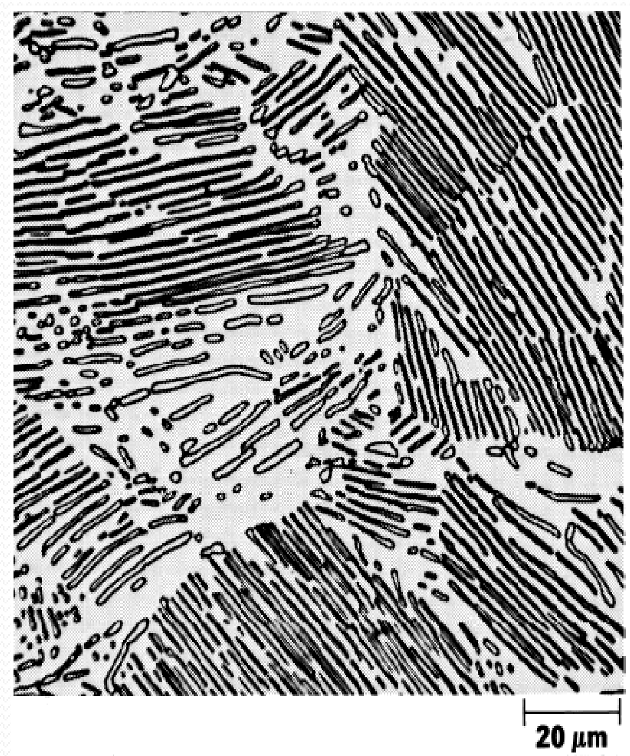
Eutectoid Reaction

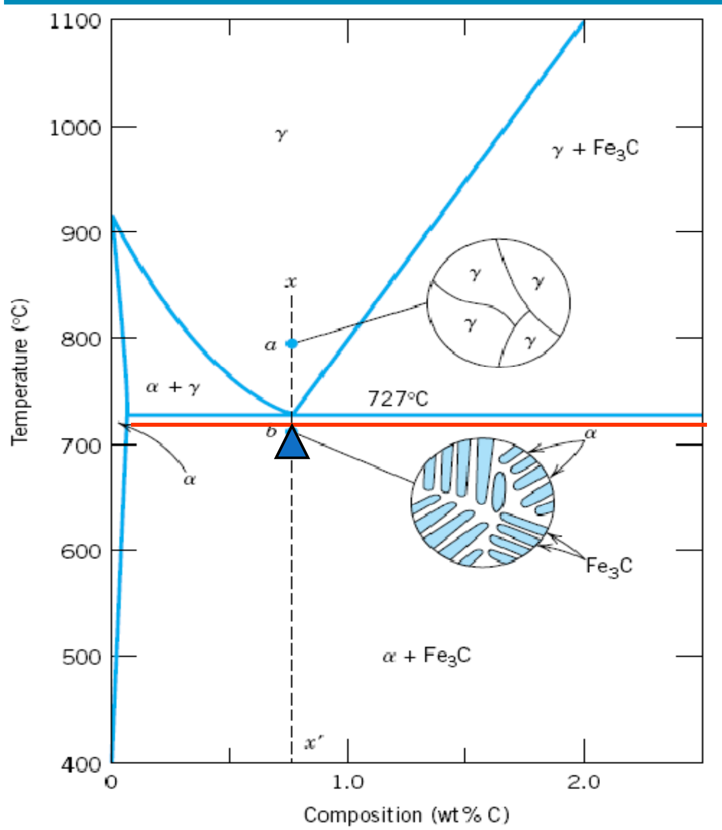
$$\gamma\ (0.8\ wt\%\ C) \xrightarrow{725^o C} \alpha\ (0.02\ wt\%\ C) + Fe_3C\ (6.67\ wt\%\ C)$$



Eutectoid Reaction

$$\underset{0.8}{\gamma} \xrightarrow[\text{cool}]{725\,^{o}C} \underbrace{\underset{0.02}{\alpha} + \underset{6.67}{Fe_3C}}_{\text{Pearlite}}$$



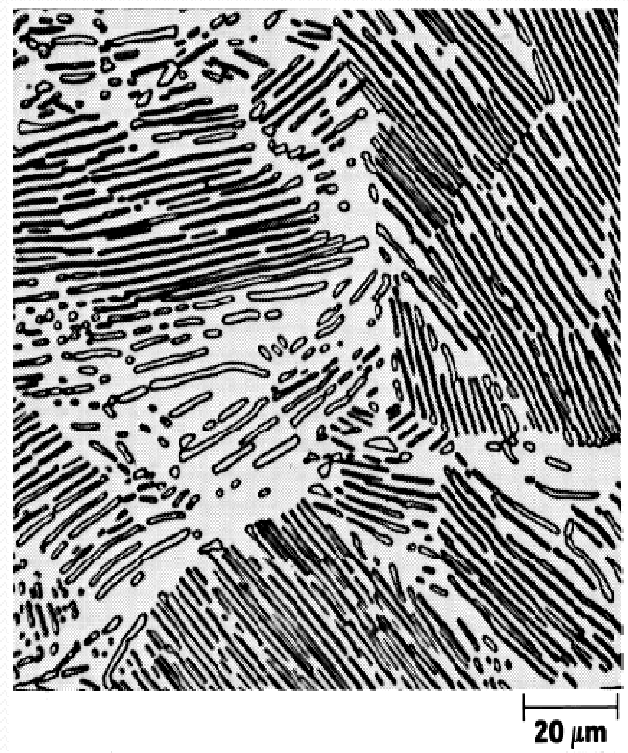


Eutectoid Reaction

$$\gamma \xrightarrow[\text{cool}]{725\ ^{o}C} \alpha + Fe_3C$$

0.8 0.02 6.67

Pearlite

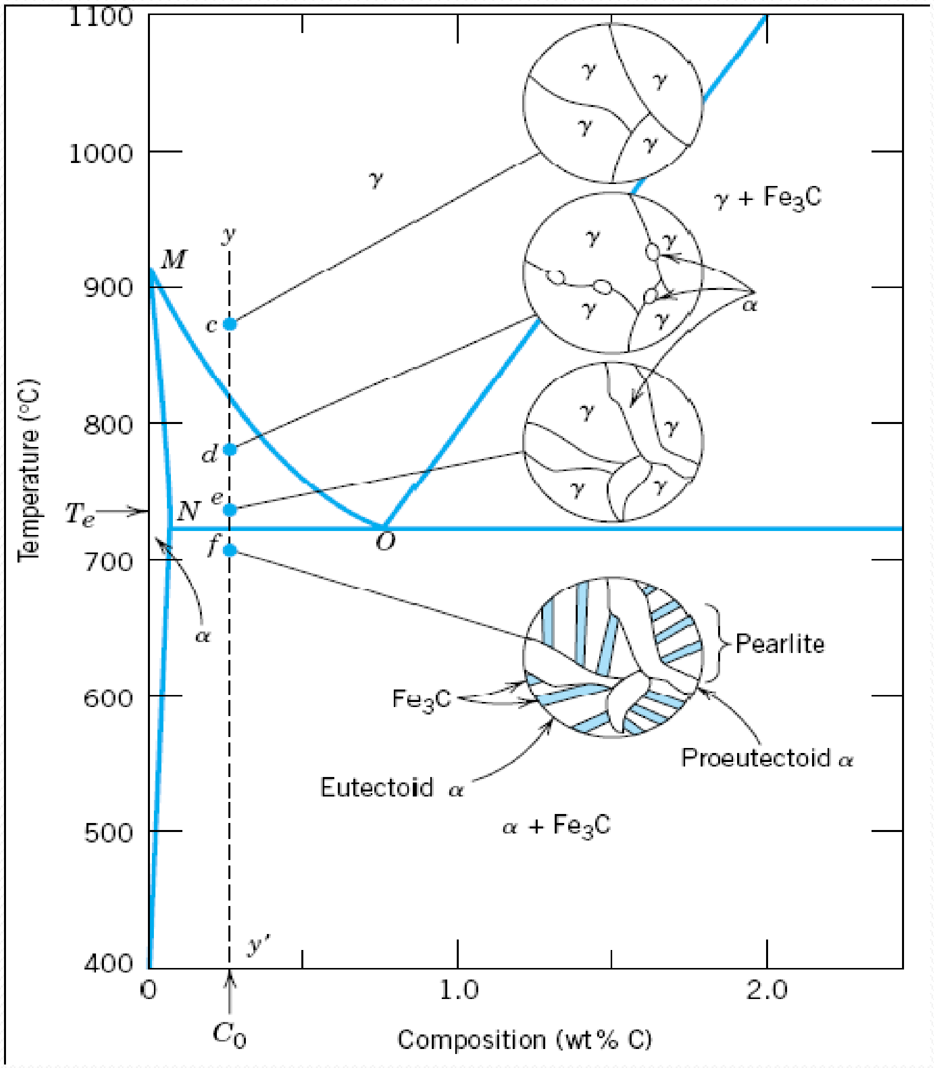


Ammount of Fe_3C in Pearlite

Red Tie Line below eutectoid temp

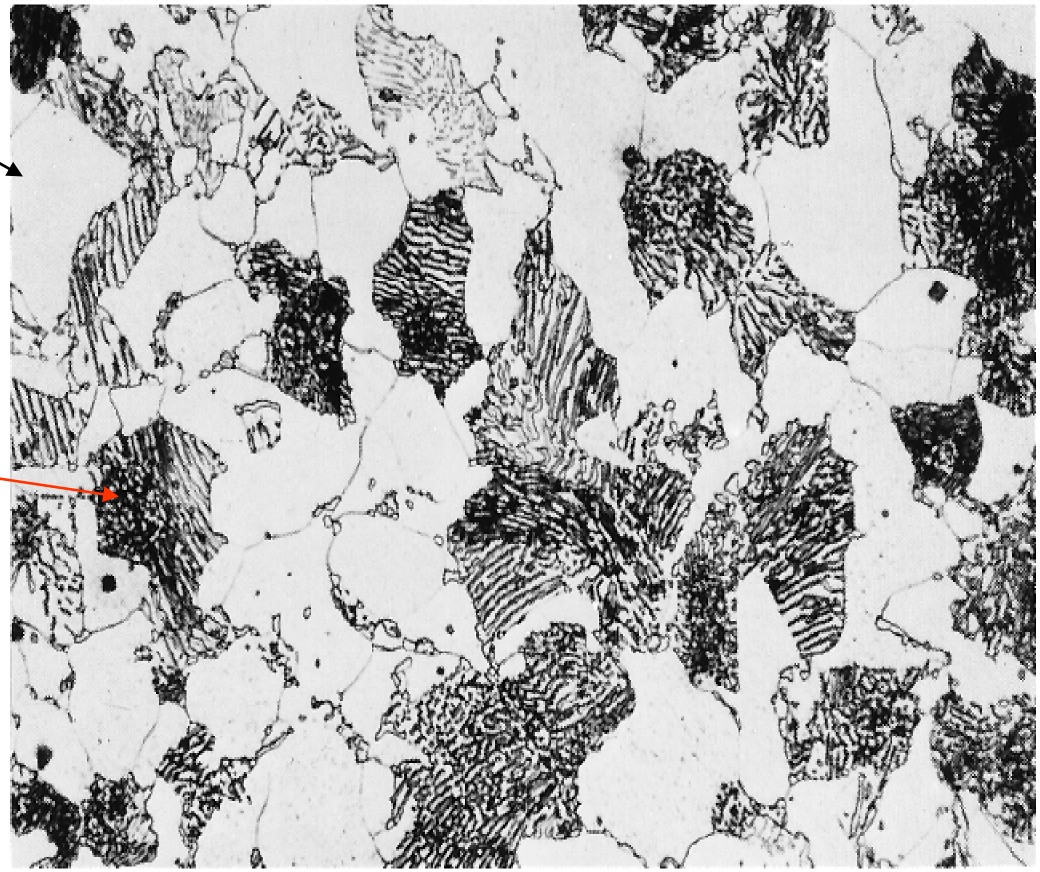
$$f_{F_3C}^{pearlite} = \frac{0.8-0.02}{6.67-0.02} = \frac{0.78}{6.65} = 0.117$$

Development of Microstructure in a hypoeutectoid steel

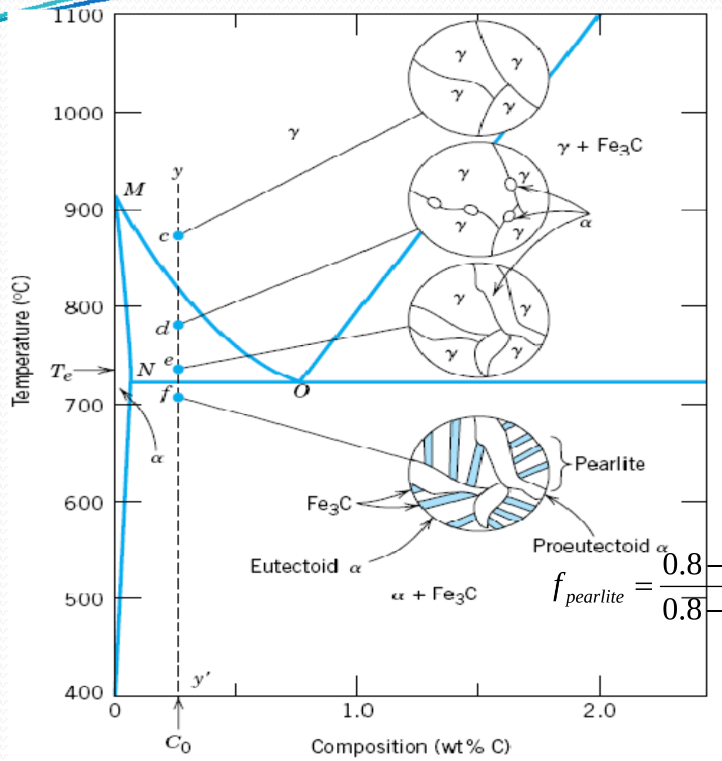


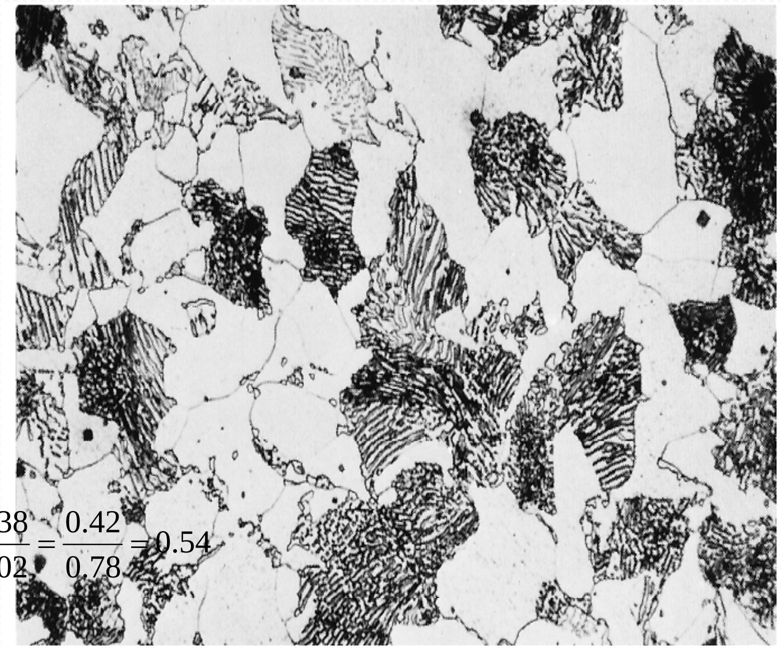
Proeutectoid Ferrite

Pearlite



Microsructure of a hypoeutectoid steel, 0.38 wt% C



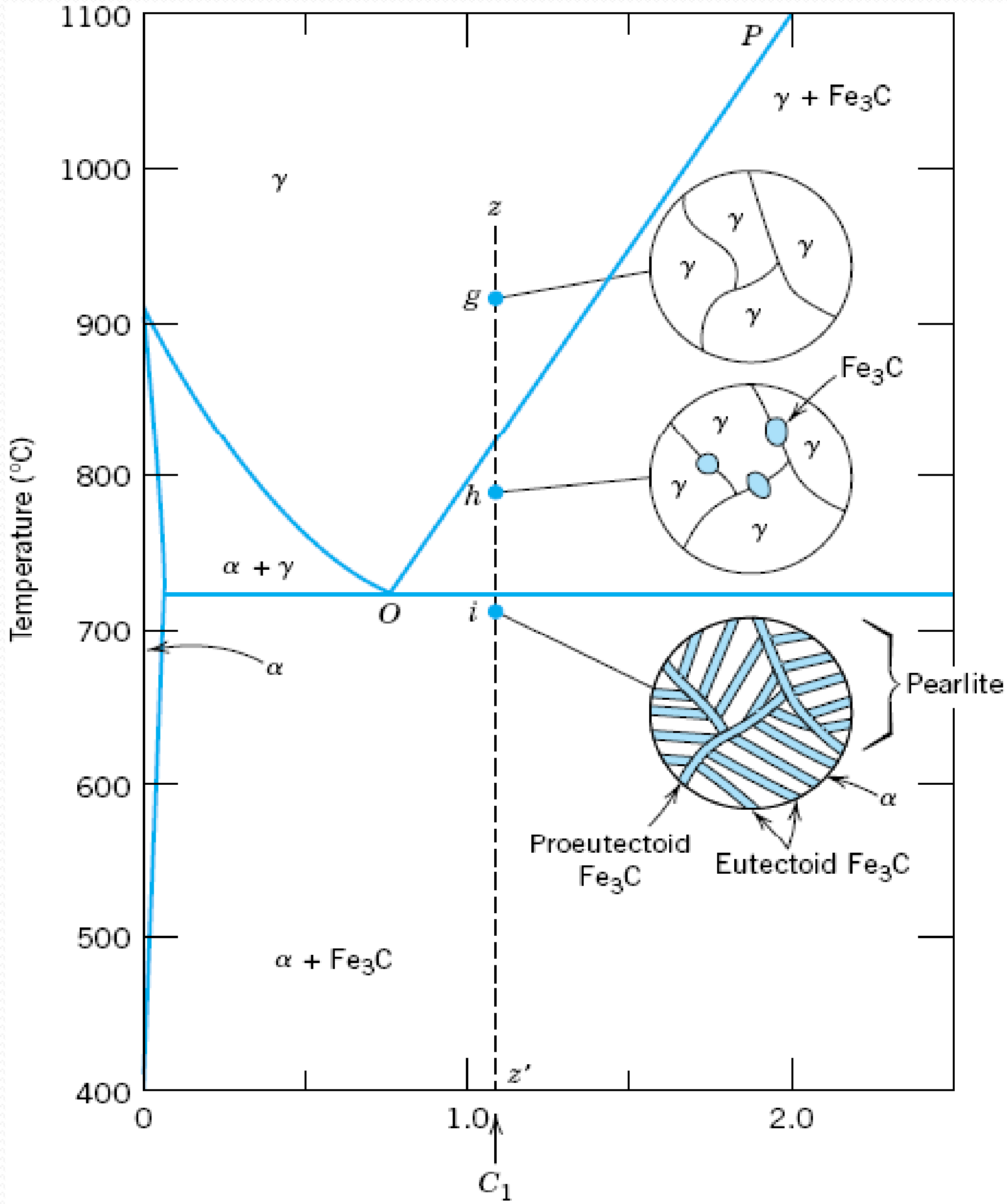


$f_{pearlite}$ below T_E = $f_{austenite}$ above T_E

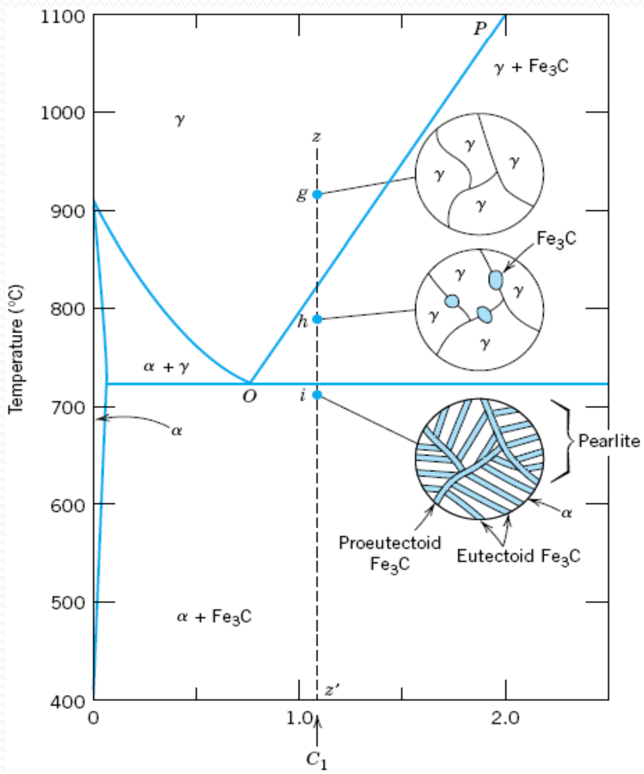
Tie-Line above the eutectoid temperature T_E

$$f_{pearlite} = \frac{0.8 - 0.38}{0.8 - 0.2} = \frac{0.42}{0.78} = 0.54$$

Development of Microstructure in a hypereutectoid steel



Microsructure of a hypereutectoid steel, 1.4 wt% C



$F_{proeutectoid\ cementite} = f_{cementite}$ above T_E

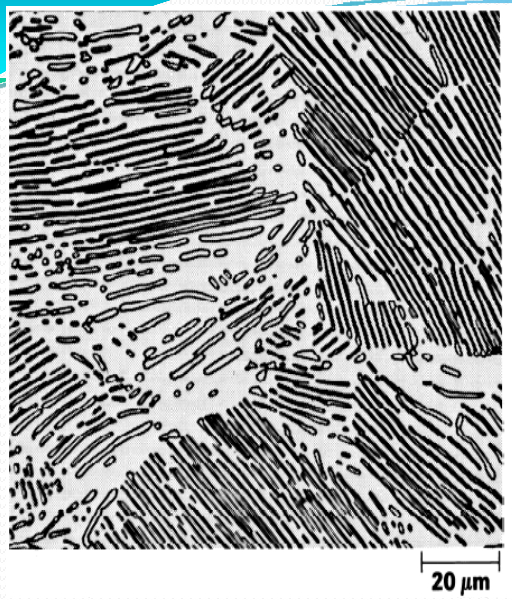
$$f_{proeutectoid\ cementite} = \frac{1.4 - 0.8}{6.67 - 0.8} = \frac{0.6}{5.87} = 0.10$$

Phase vs. microconstituents

A phase or a mixture of phases which has a distinct identity in a microstructure is called a microconstituent

Pearlite is not a phase.

It is microconstituent which is a mixture of two phases α and Fe_3C.



Eutectoid steel

α+Fe_3C

Pearlite

Hypoutectoid steel

α+Fe_3C

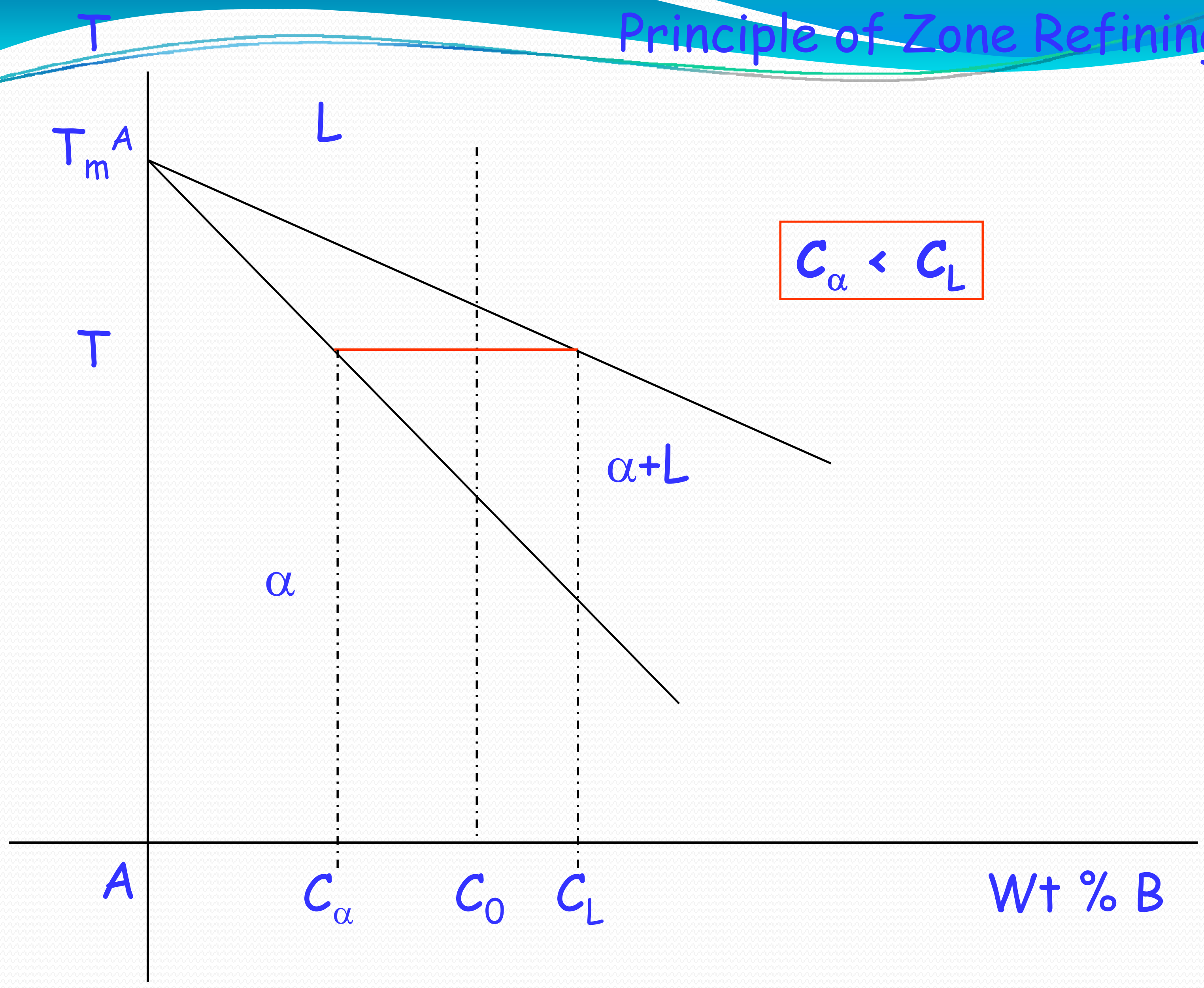
Pearlite + proeutectoid ferrite

Hypereutectoid steel

α+Fe_3C

Pearlite + proeutectoid cementite

Principle of Zone Refining



SemiconductorTransistor was invented by

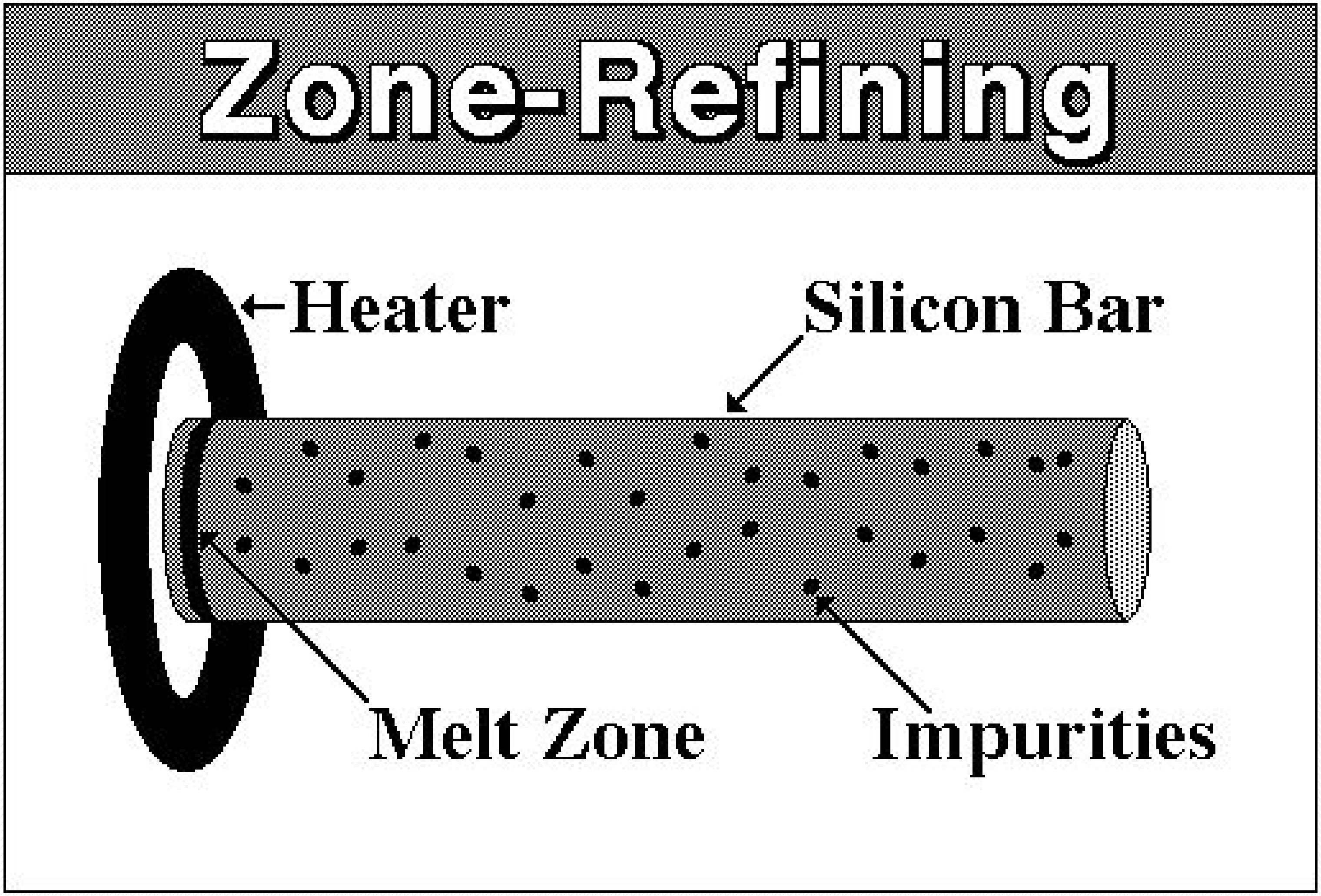
Bardeen, Brattain and Shockley

At AT&T Bell Labs

One needs ultrapure Si (impurity level few ppm)

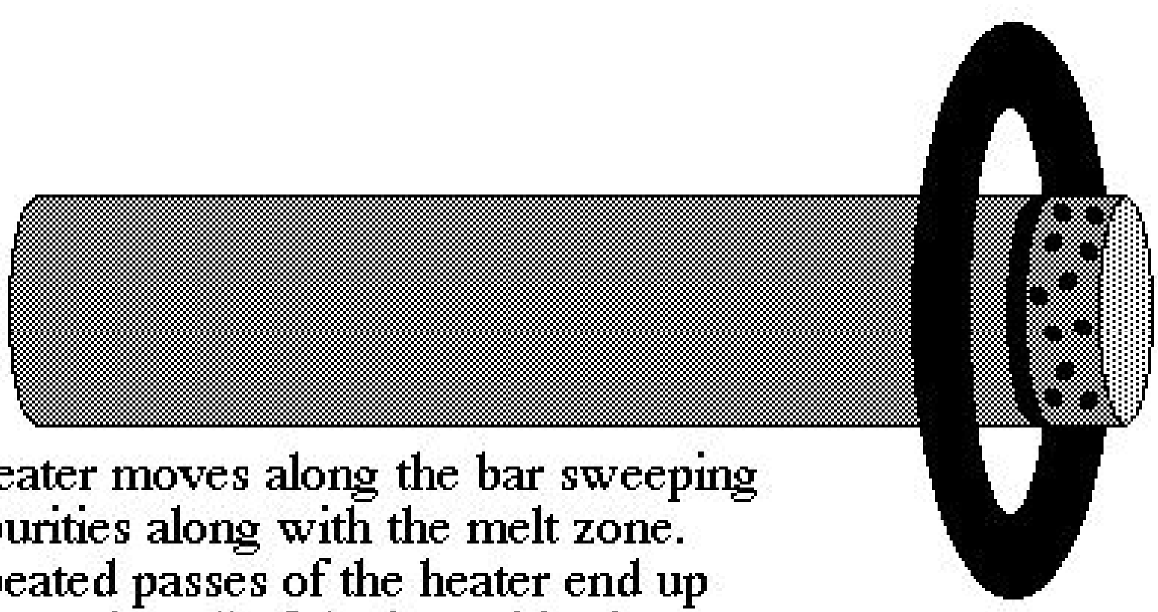
Zone Refining was invented by Pfann at Bell Labs
as a process to obtain ultrapure Si

Basis for modern Si technology



Zone-Refining
Heater
Silicon Bar
Melt Zone
Impurities

Zone-Refining



The heater moves along the bar sweeping impurities along with the melt zone. Repeated passes of the heater end up concentrating all of the impurities in one end, which is then discarded.