# Phase Diagrams

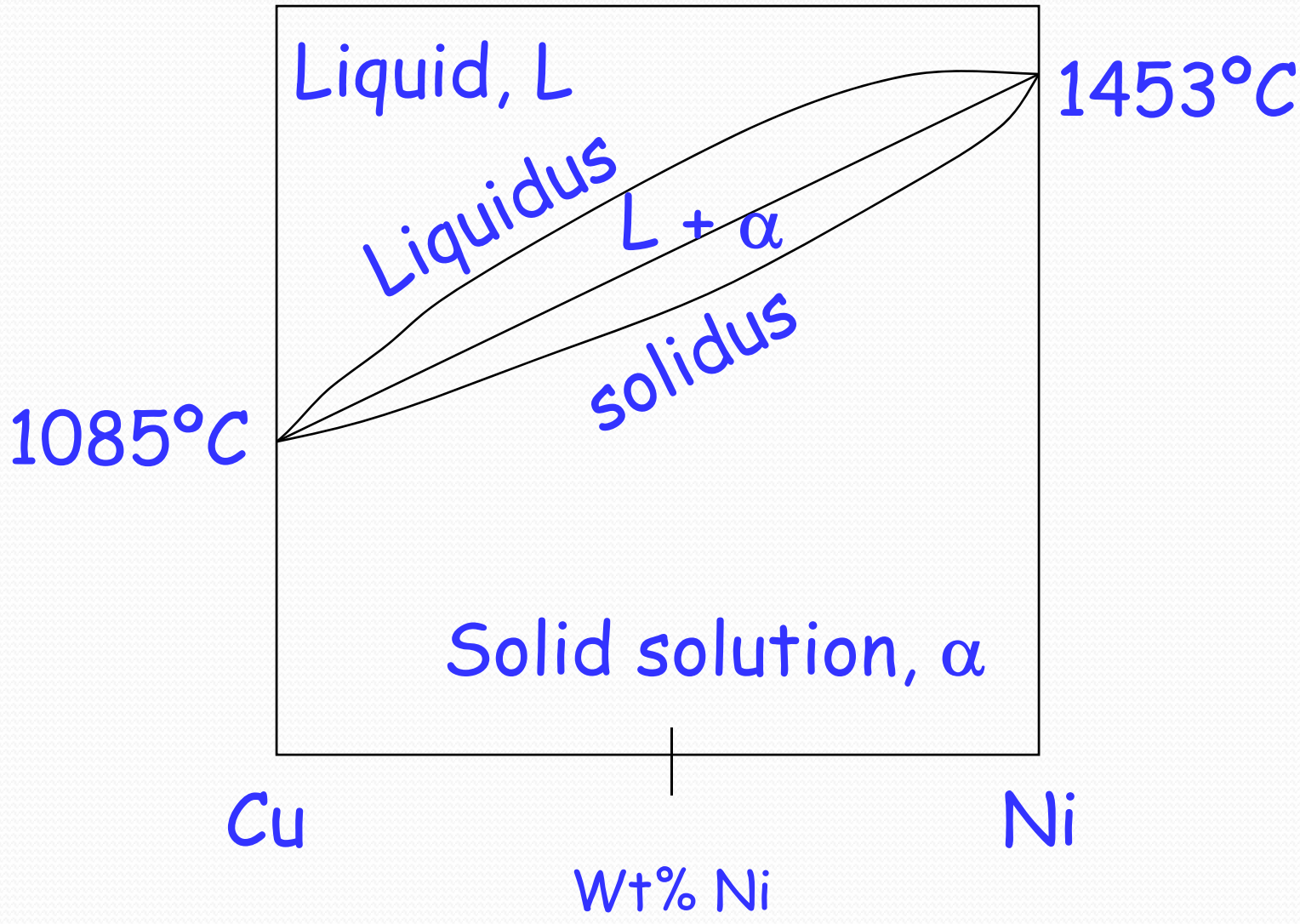
Why do cocktail ice served in expensive restaurants are clear whereas the ice formed in your refrigerator is cloudy?

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.

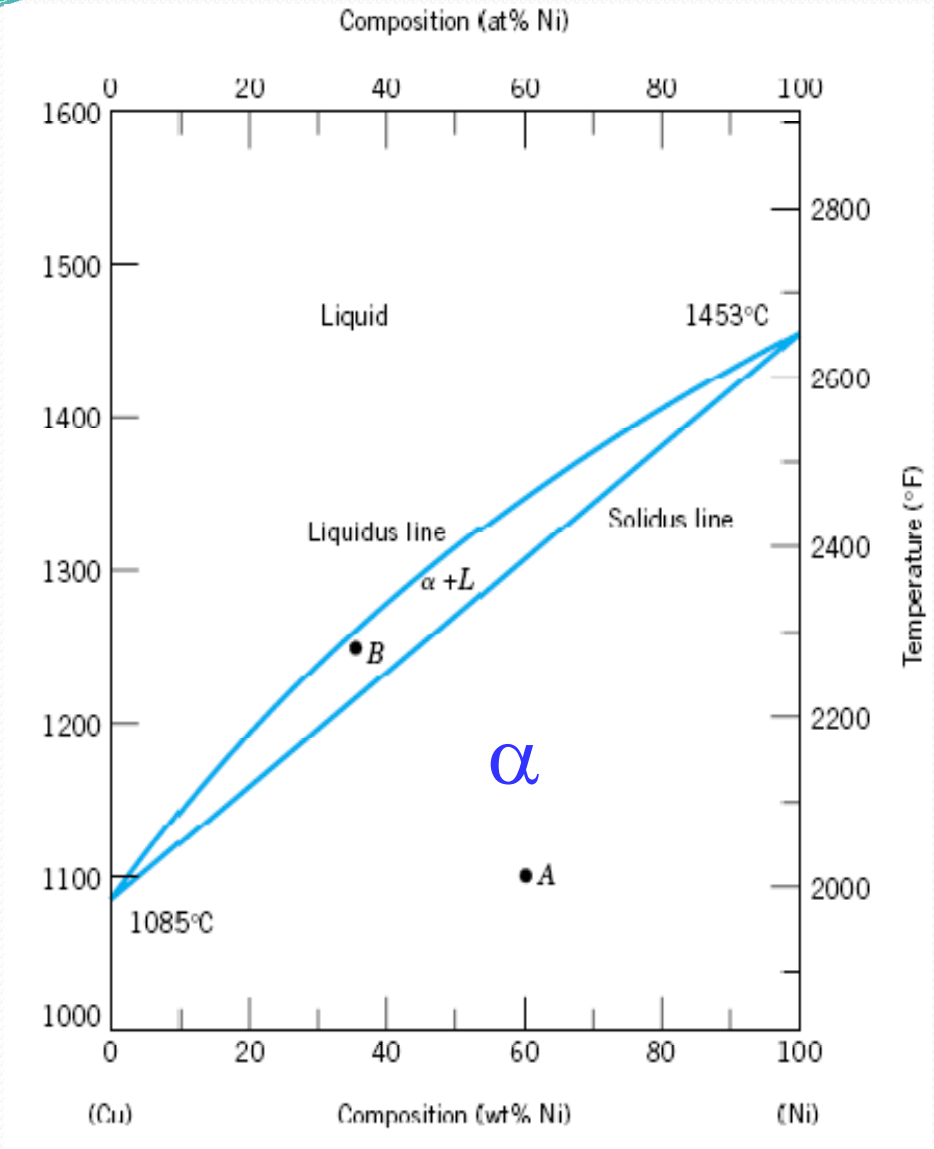
| System | components | phases |
|---|---|---|
| Water | $H_2O$ | liquid |
| Water +ice | $H_2O$ | Liquid+solid |
| shikanji | nimbu, chini and pani | liquid solution |
| Mild steel | Fe + C | $\alpha + Fe_3C$ |

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

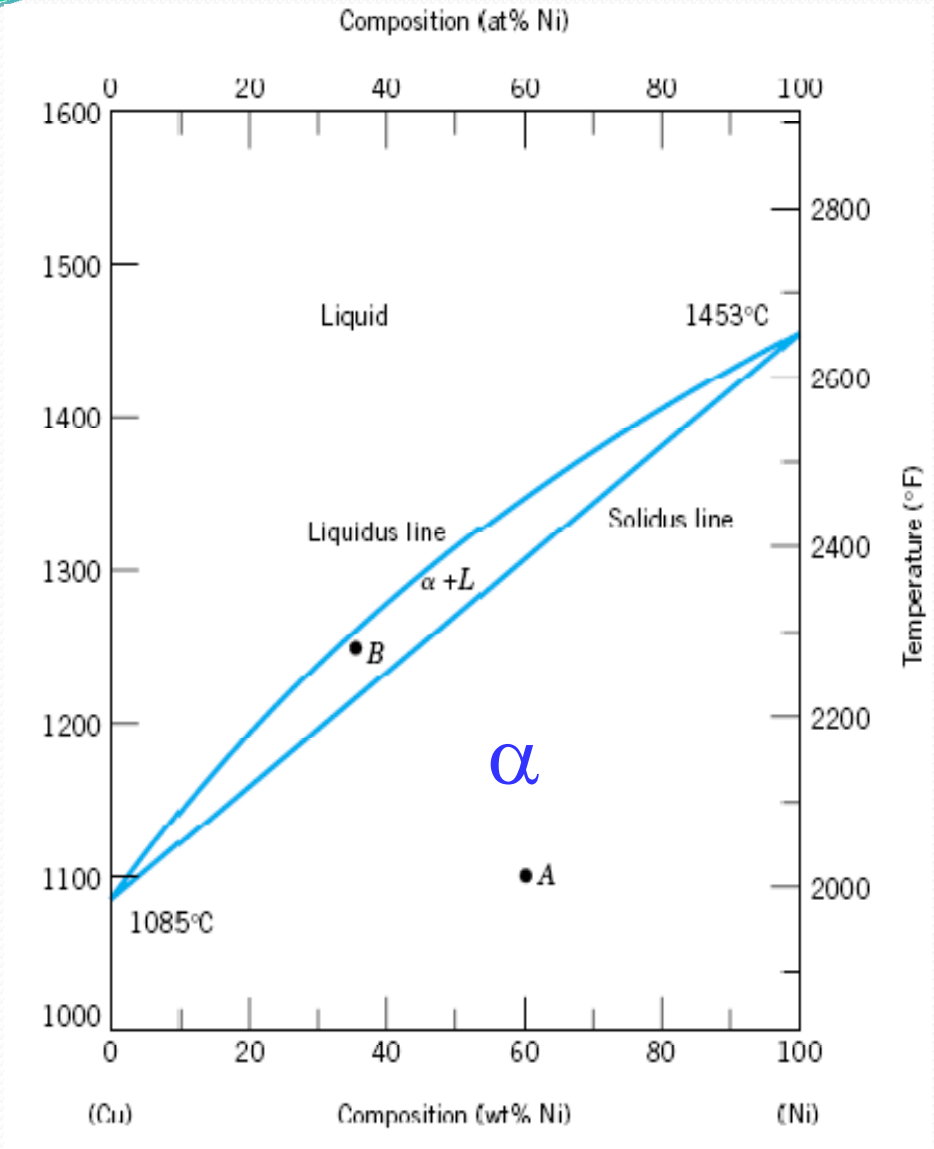
# Phase Diagrams

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 ?**

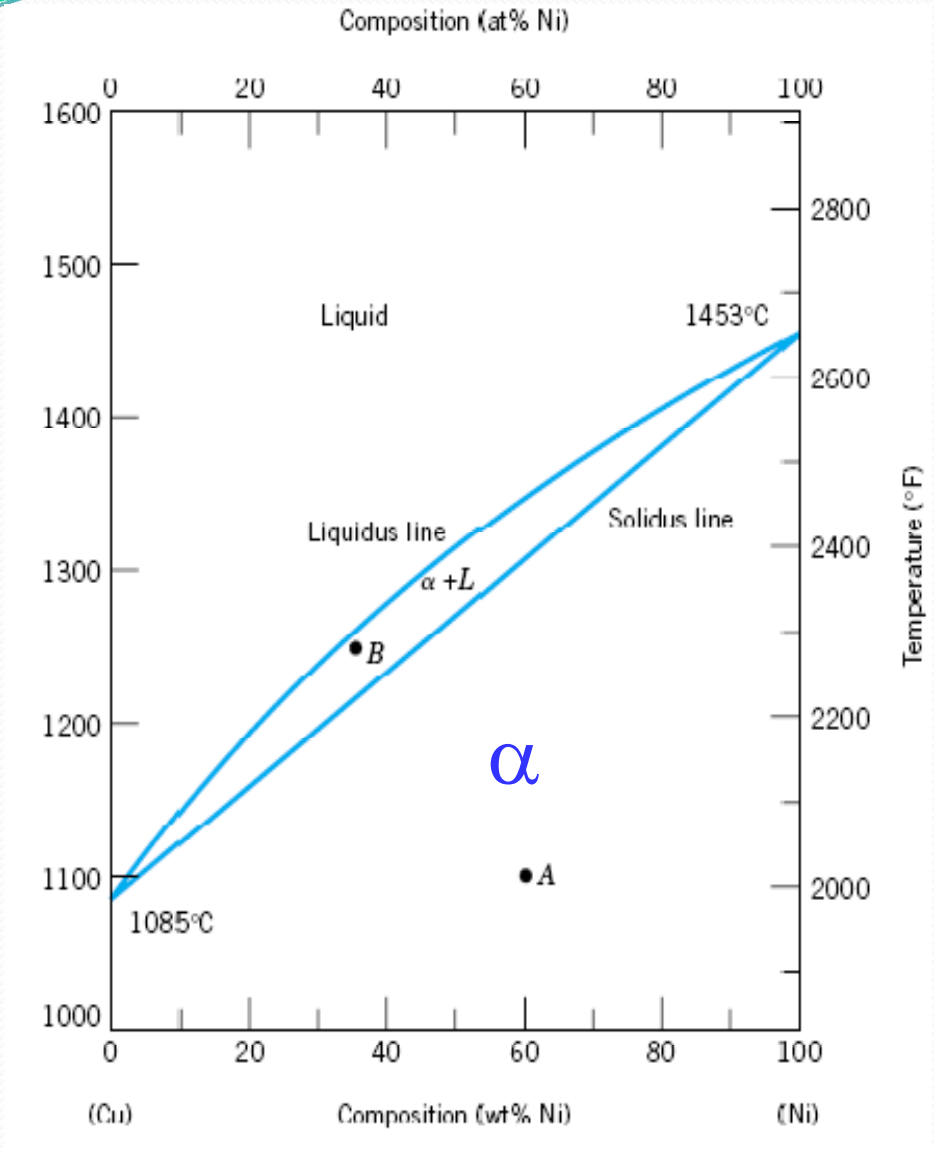
Ans: 60 wt%Ni

**Q: Phase amount ?**

Ans: 100%

## Point B:

35 wt% Ni at 1250°C




**Q: Phases present?**

Ans: $\alpha + L$

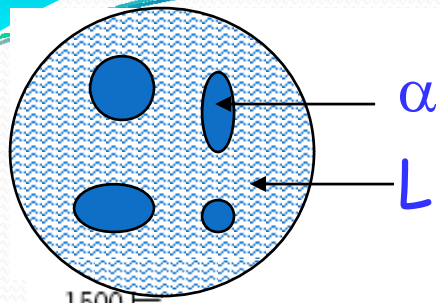
**Q: Phase compositions ?**

Tie Line Rule

**Q: Phase amounts ?**

Lever Rule

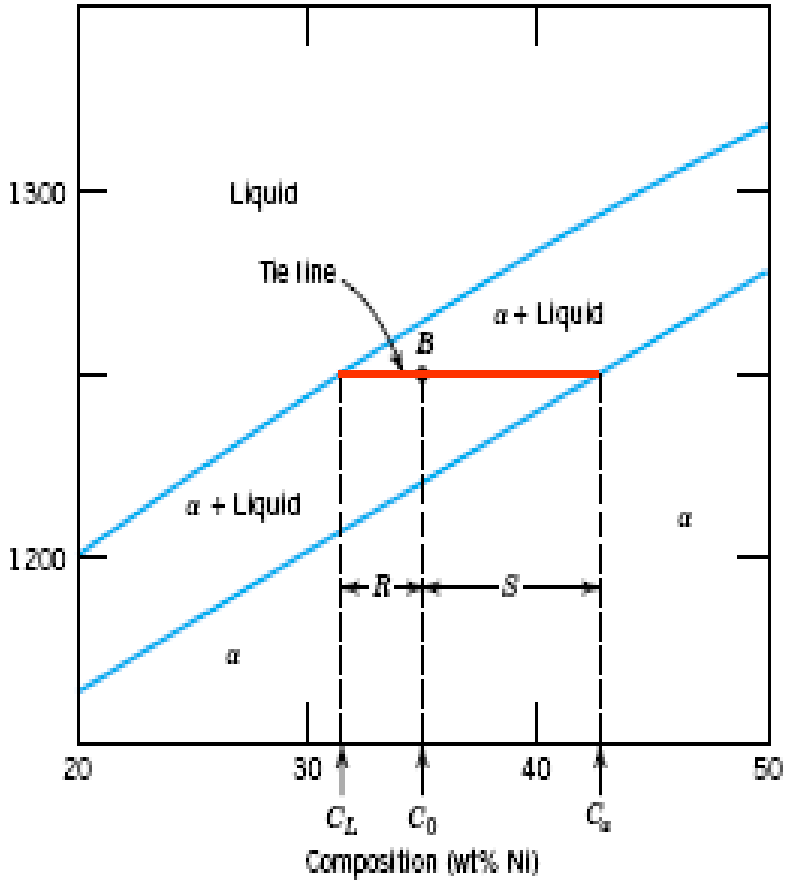
# Composition of phases in the two-phase region







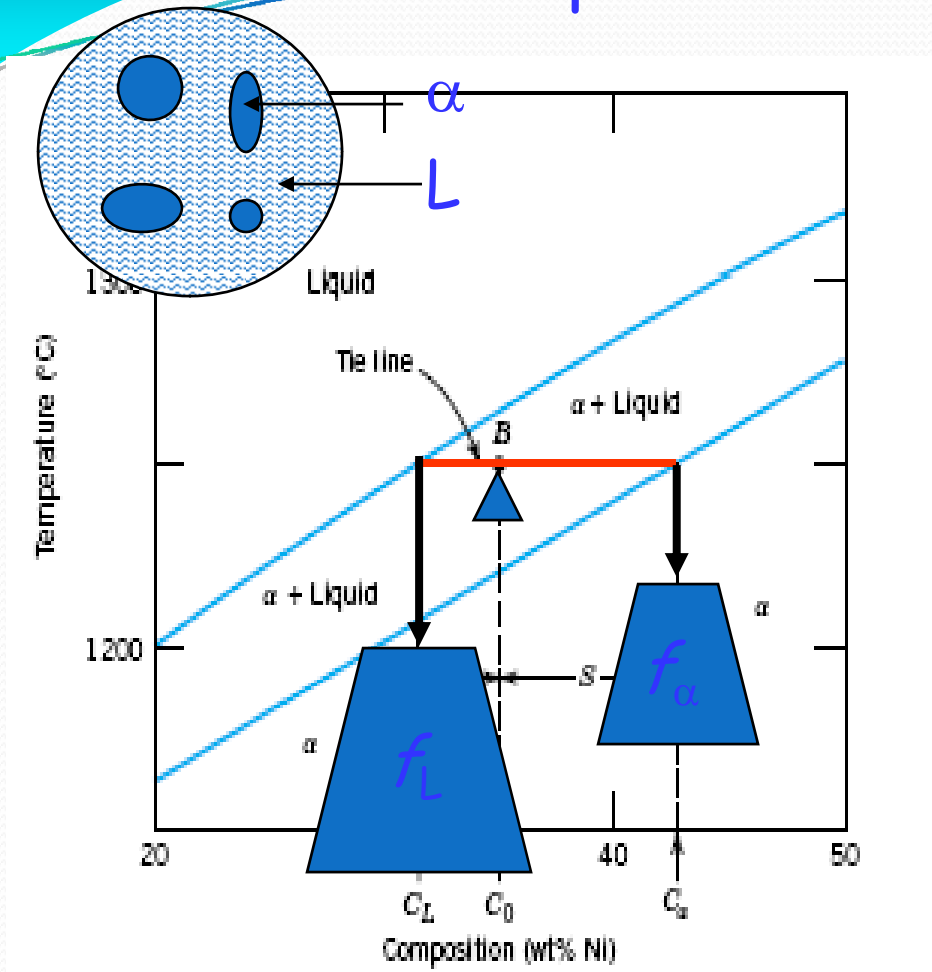
## Tie Line Rule




$C_L$ = 31.5 wt% Ni

$C_\alpha$ = 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

$f_\alpha$: weight at solidus point

## The lever is balanced

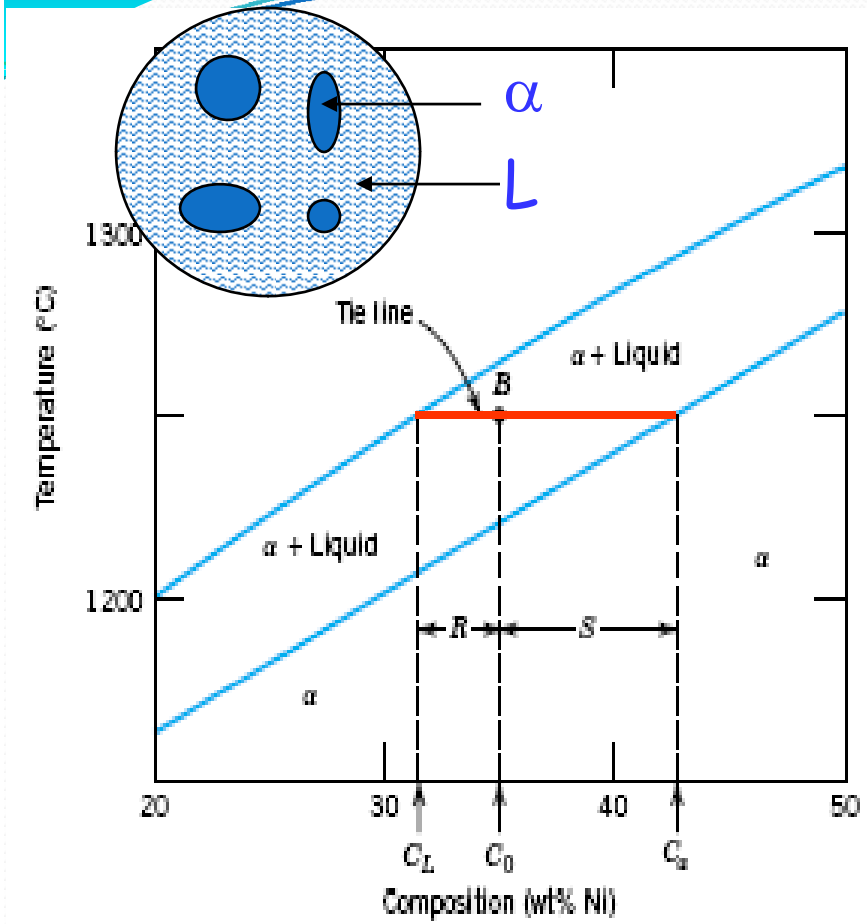
$$f_L(C_0 - C_L) = f_\alpha(C_\alpha - C_0)$$

$$f_L + f_\alpha = 1$$

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 = $f_L\, W C_L/100$

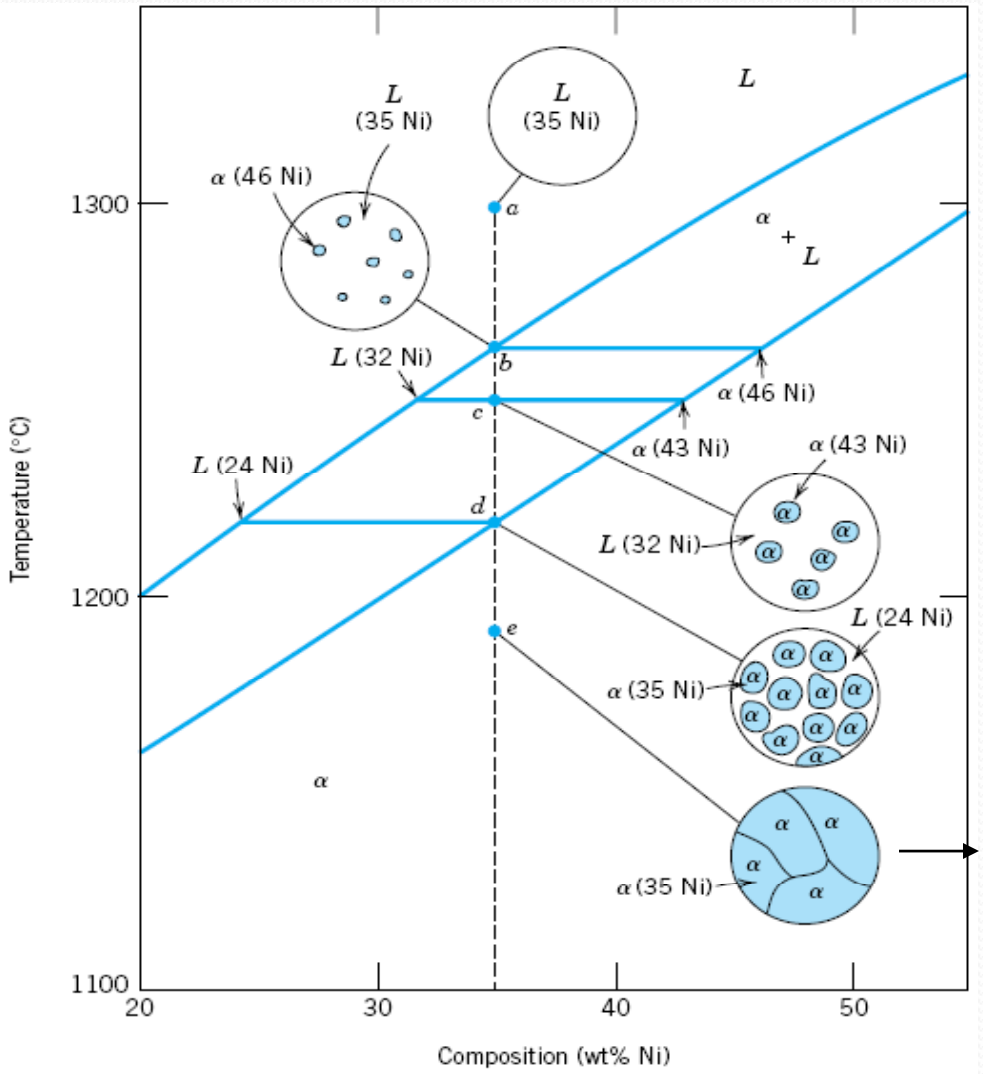
**Wt of Ni in alloy = Wt of Ni in α + Wt of Ni in L**

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

$$f_\alpha + f_L = 1$$

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

# 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

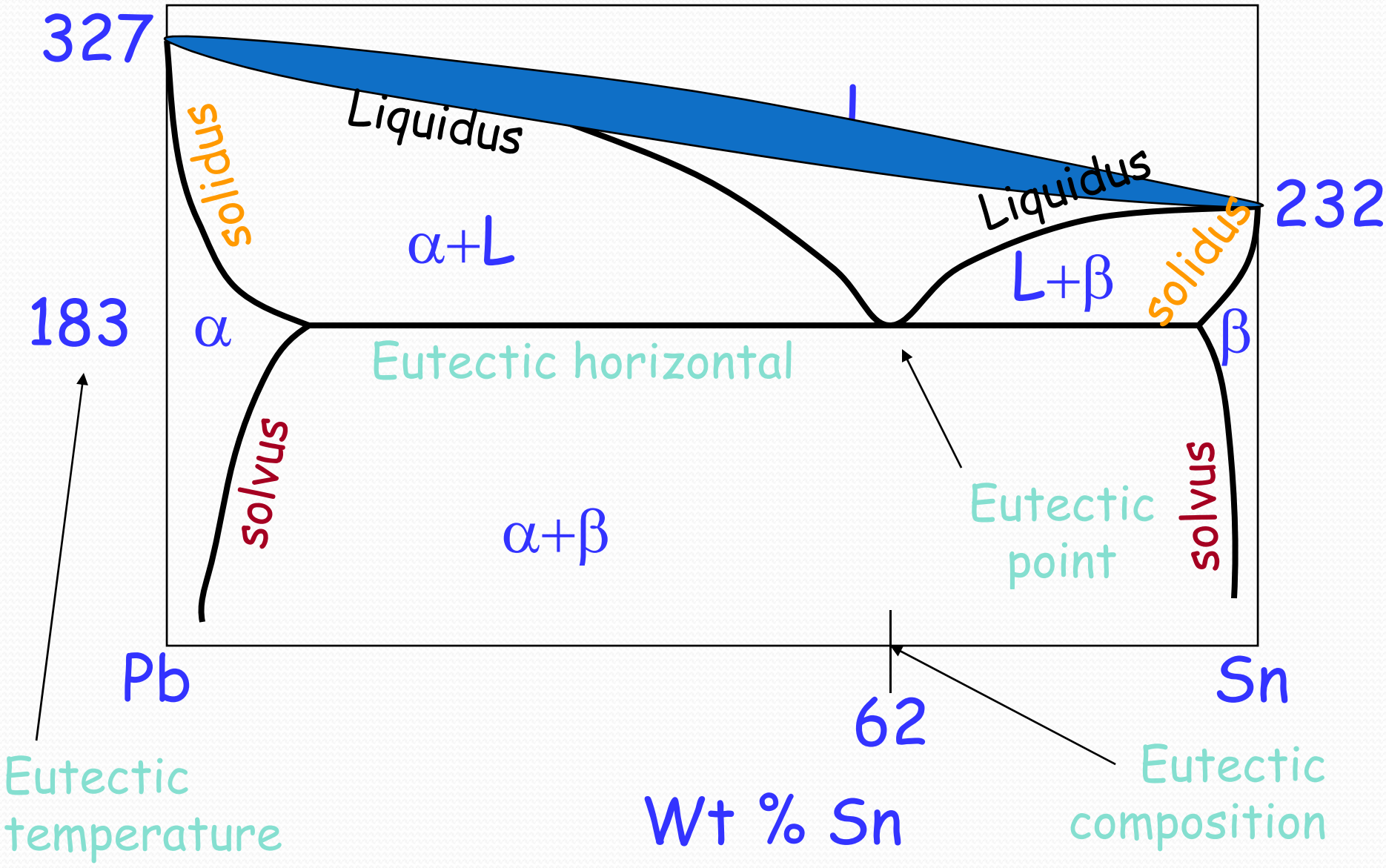
What is best composition of the solder alloy?

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

$\alpha$: Pb rich substitutional solid solution of Pb and Sn

crystal structure: monatomic FCC

$\beta$: Sn rich substitutional solid solution of Pb and Sn

crystal structure: monatomic BCT

## Woods metal tea party

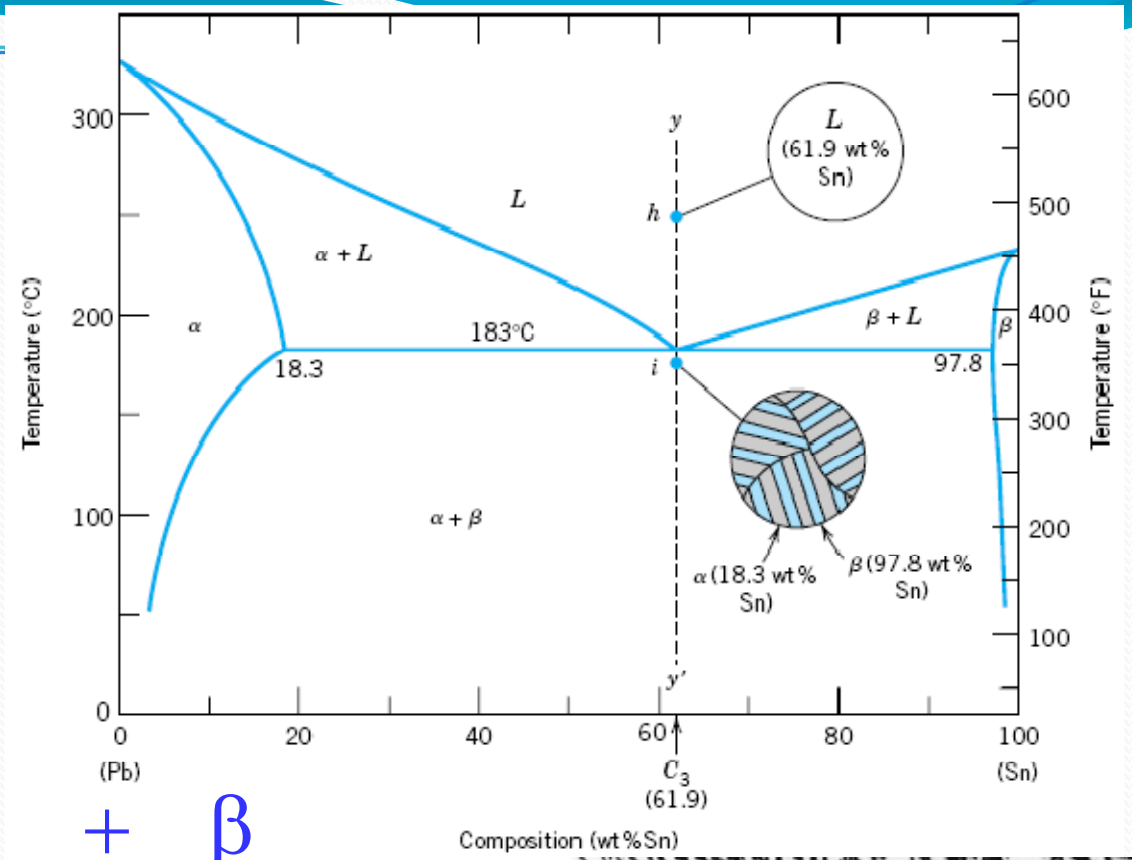
Bi 50.0 wt%
Pb 25.0 wt%
Cd 12.5 wt%
Sn 12.5 wt%

An eutectic alloy with m.p. of 70°C

100 g US$ 181

Anti-Fire Sprinklers

# Eutectic reaction



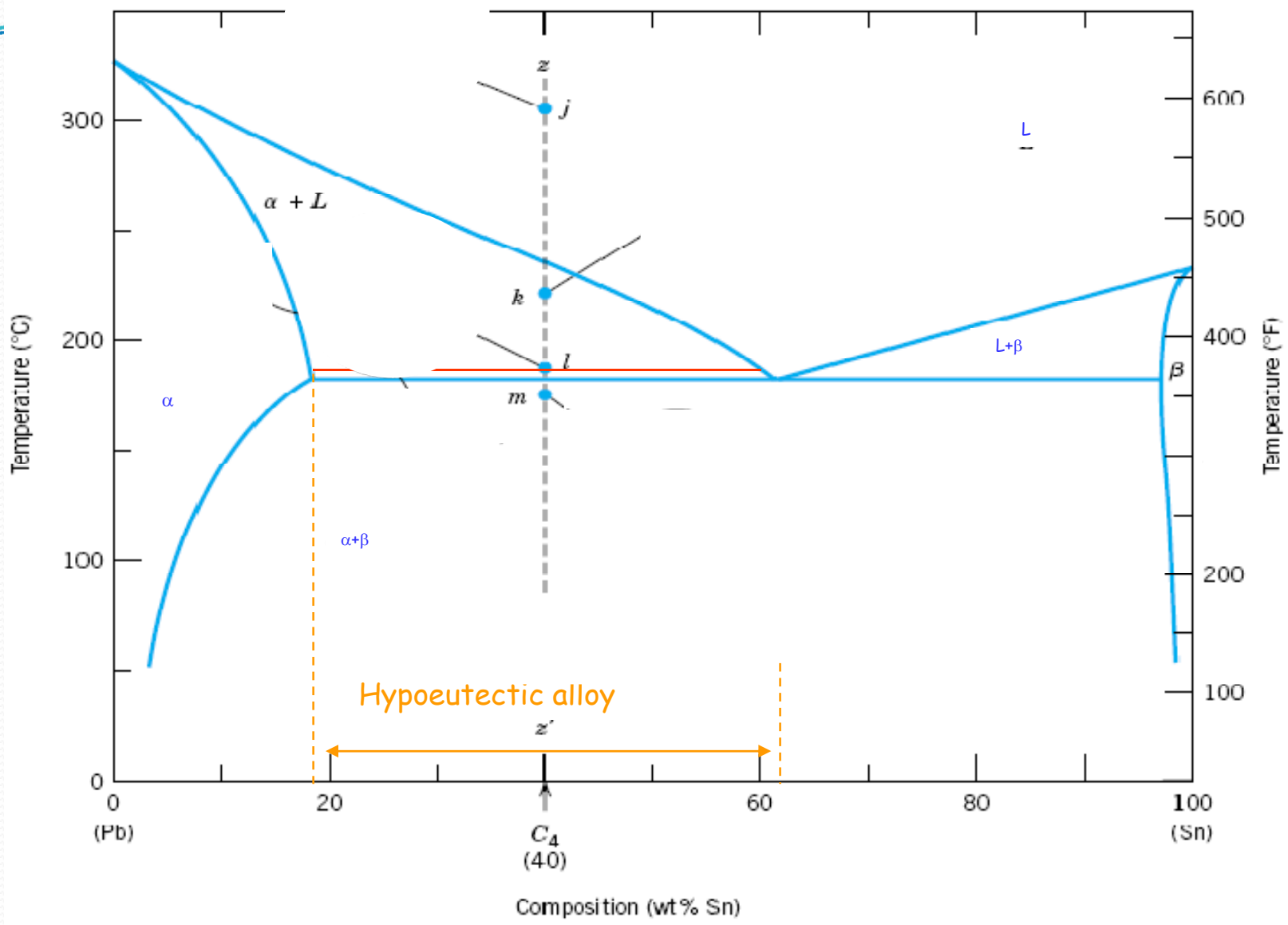

## Invariant reaction

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

62 wt%Sn → 18 wt%Sn + 97 wt%Sn

Eutectic mixture

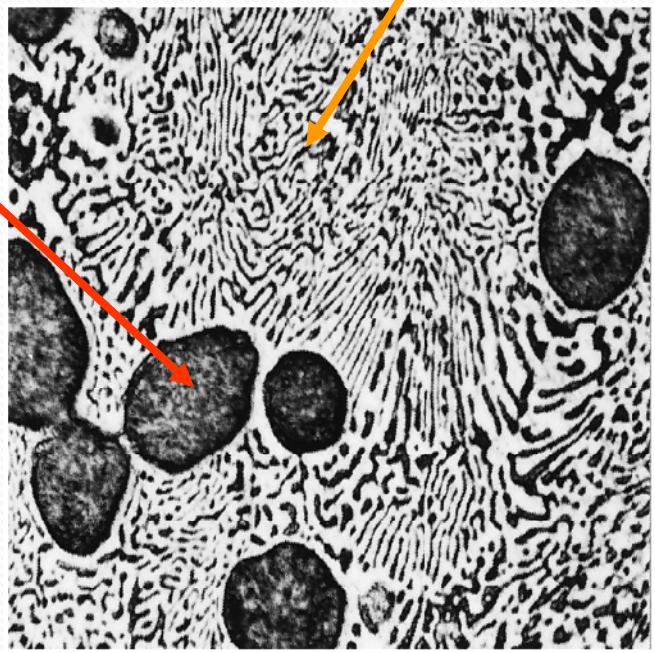
Callister Figs. 9.11, 12 375 X

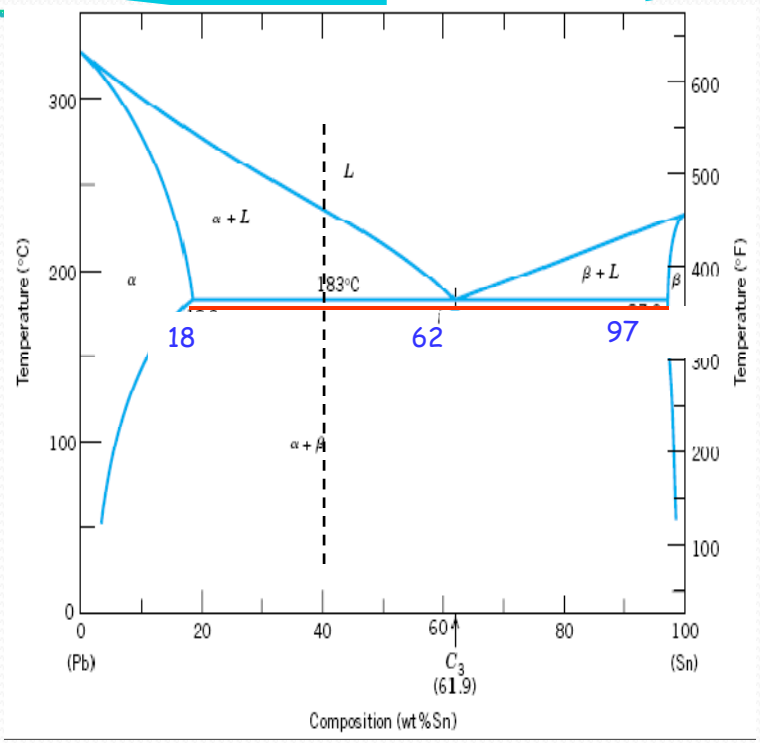



# Microstructure of hypoeutectic alloy

Eutectc mixture α+β

Proeutectic or Primary α





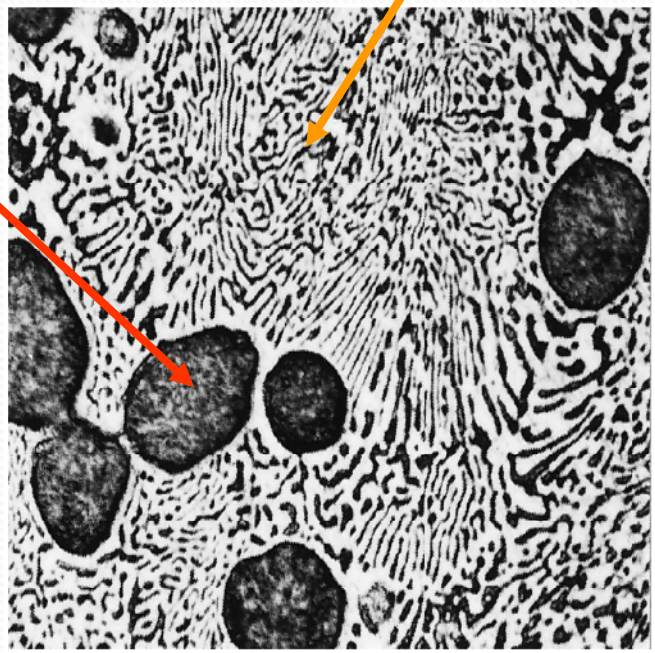

Amount of total α and total β at a temperature just below 183°C

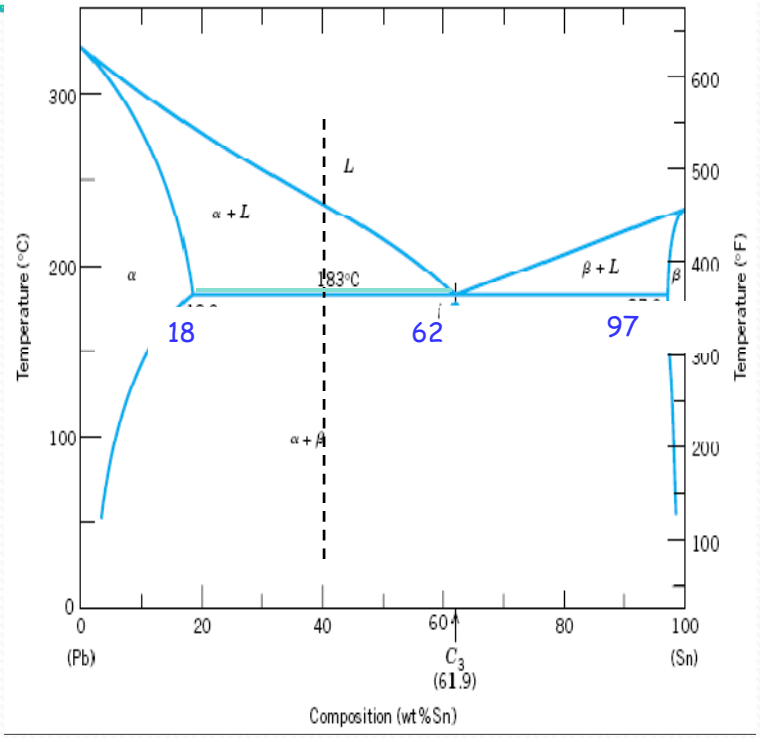
Tie line just below 183°C (red)

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

Eutectc mixture α+β

Proeutectic or Primary α





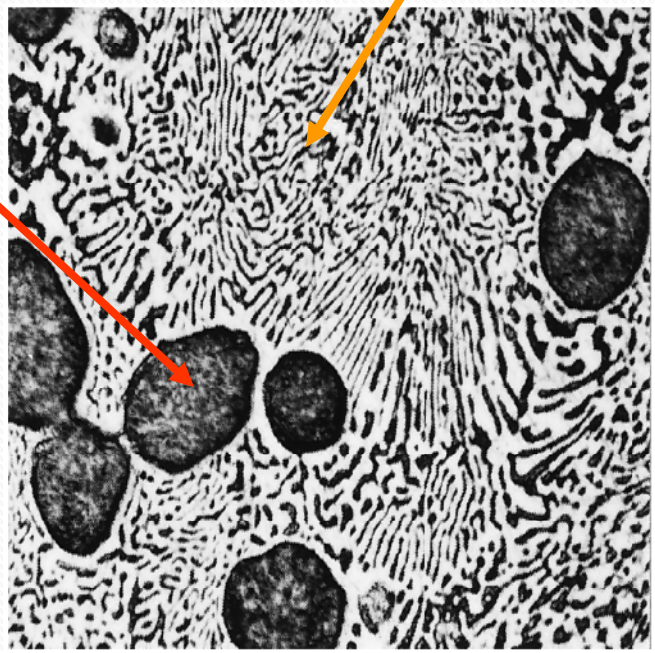

Amount of proeutectic α at a temperature just below 183°C

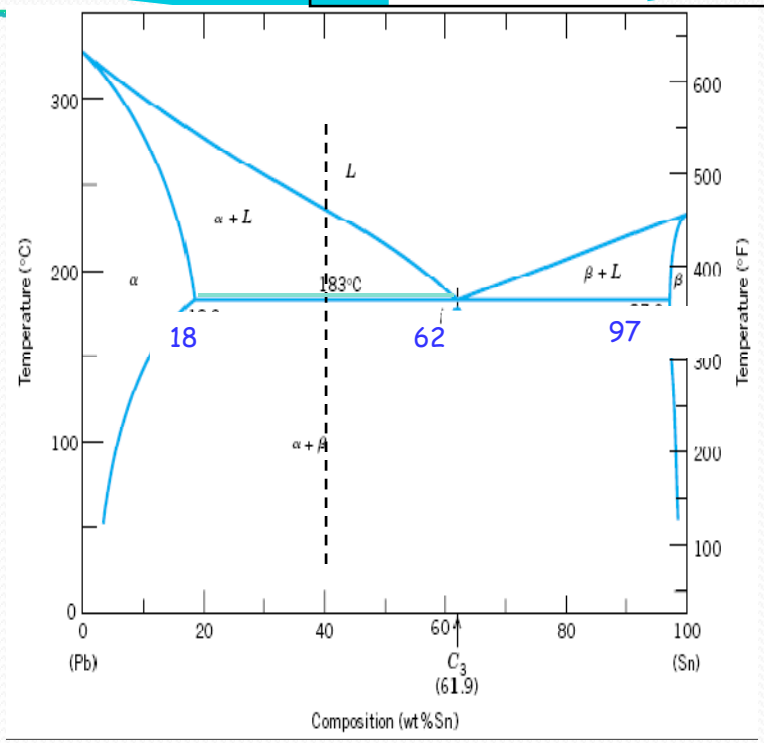
= Amount of α at a temperature just above 183°C

Tie line just above 183°C (green)

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

# EXPERIMENT 5



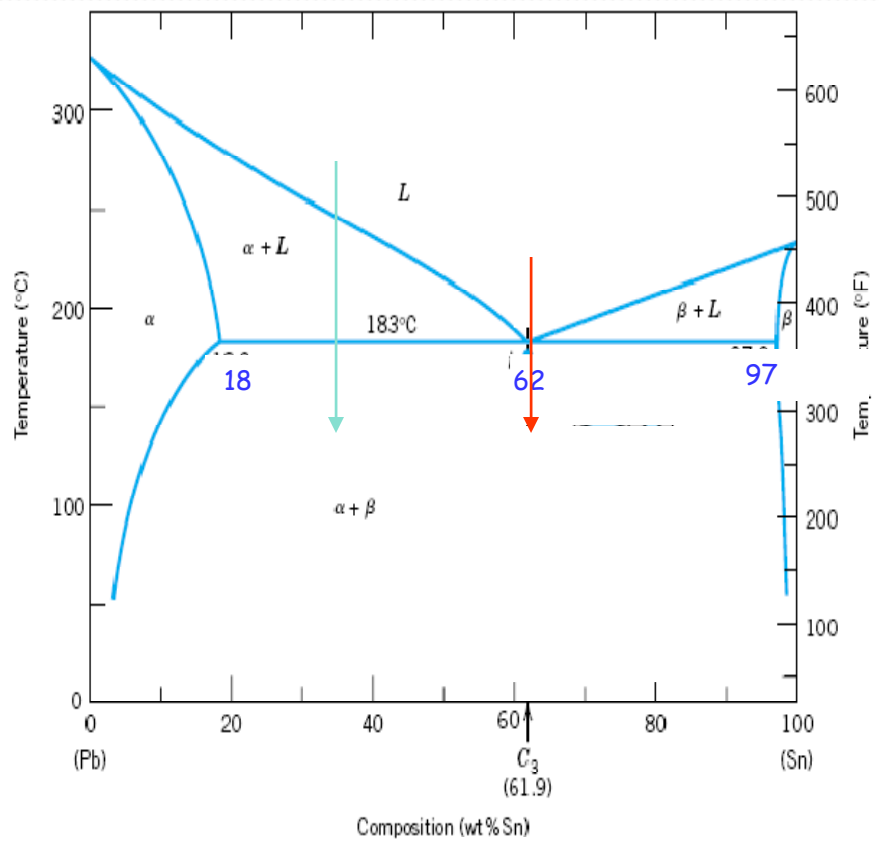

Let the fraction of proeutectic α in micrograph $f_{pro\ \alpha} = 0.25$

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 $\alpha$+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

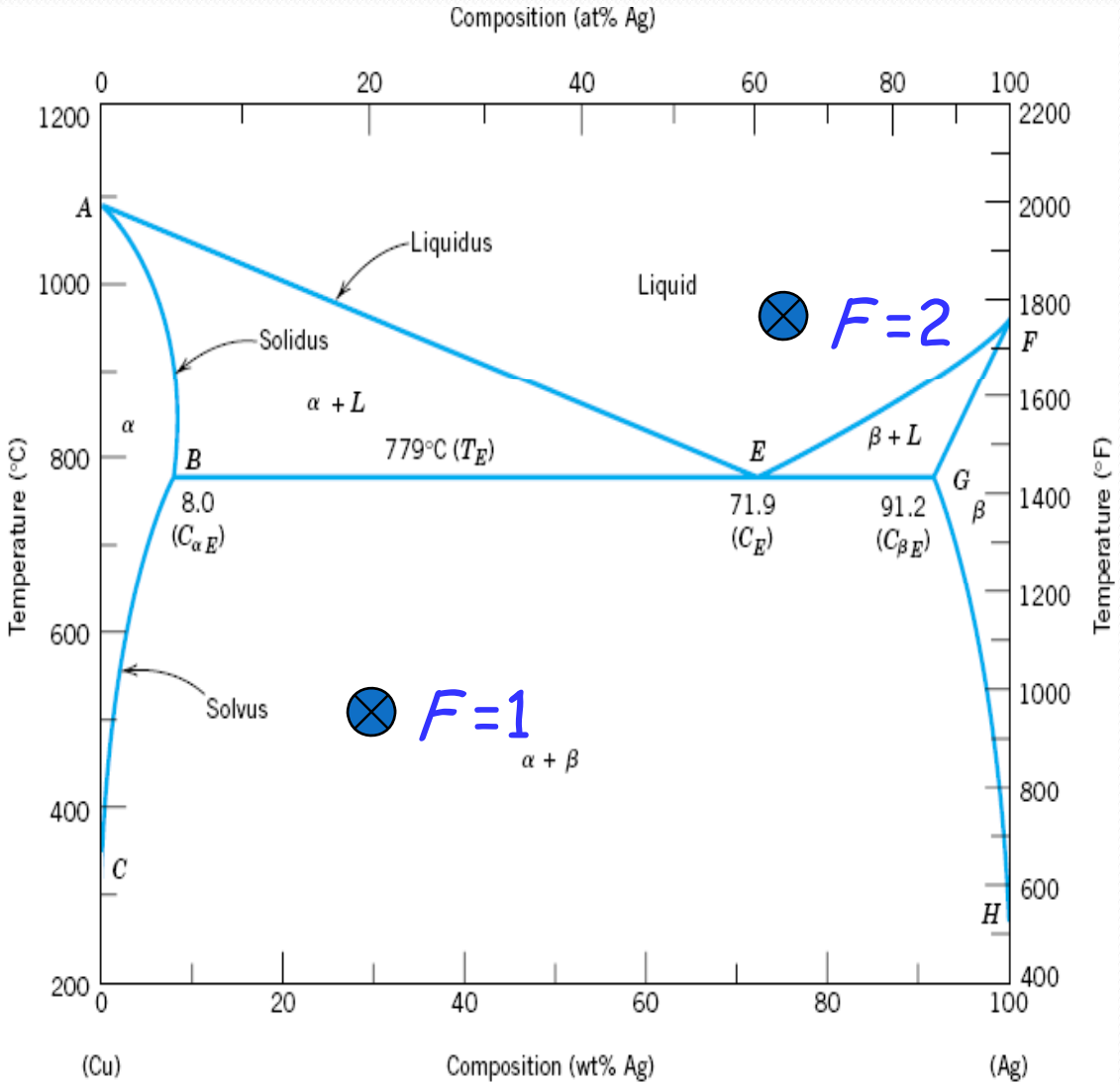
$$F = C - P + 2$$

If pressure and temp both are variables

$$F = C - P + 1$$

If pressure is held constant

$$F = C - P + 1$$




F=2

F=1

C=2

F=3-P

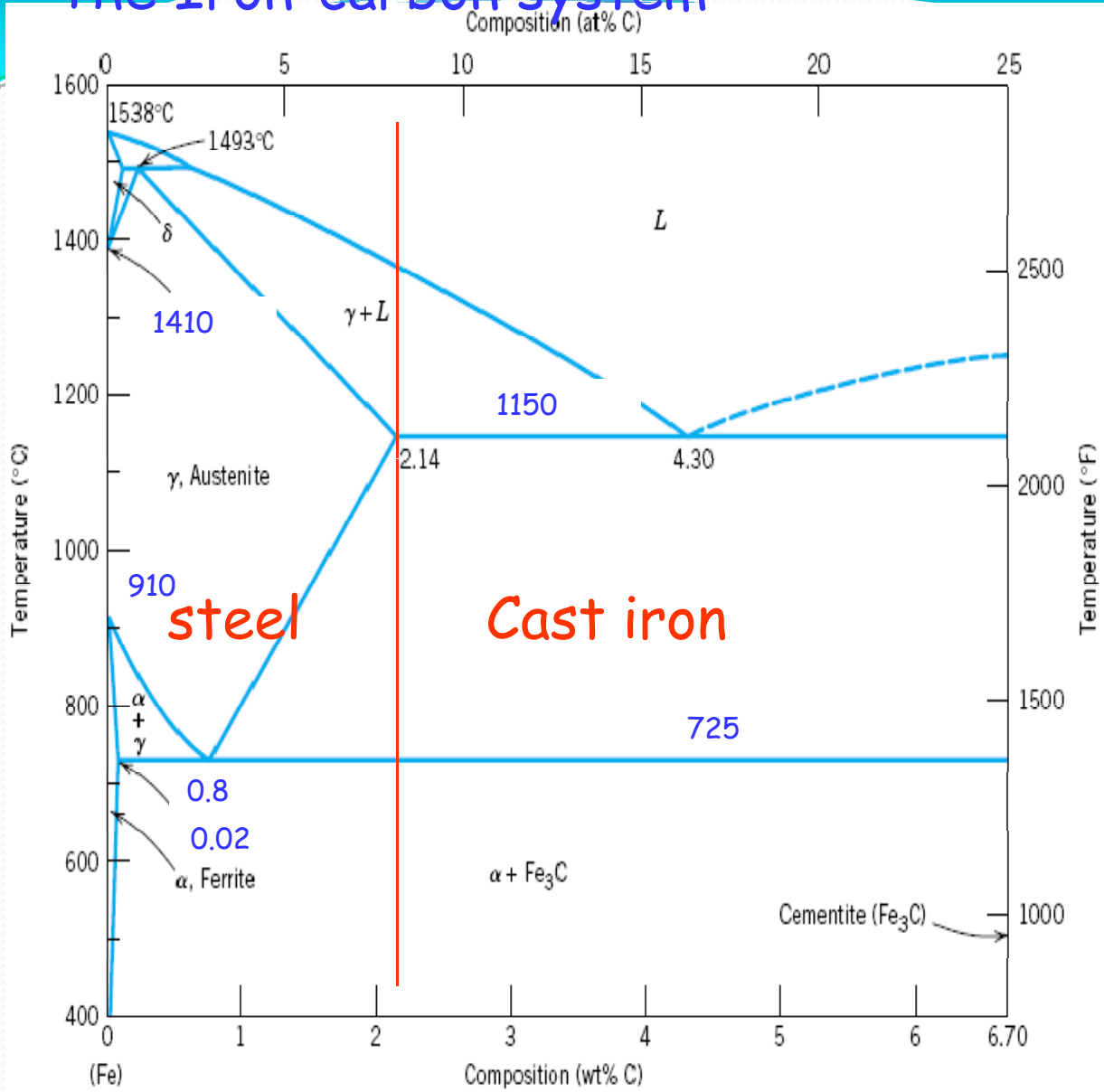
At eutectic reaction P=3

(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

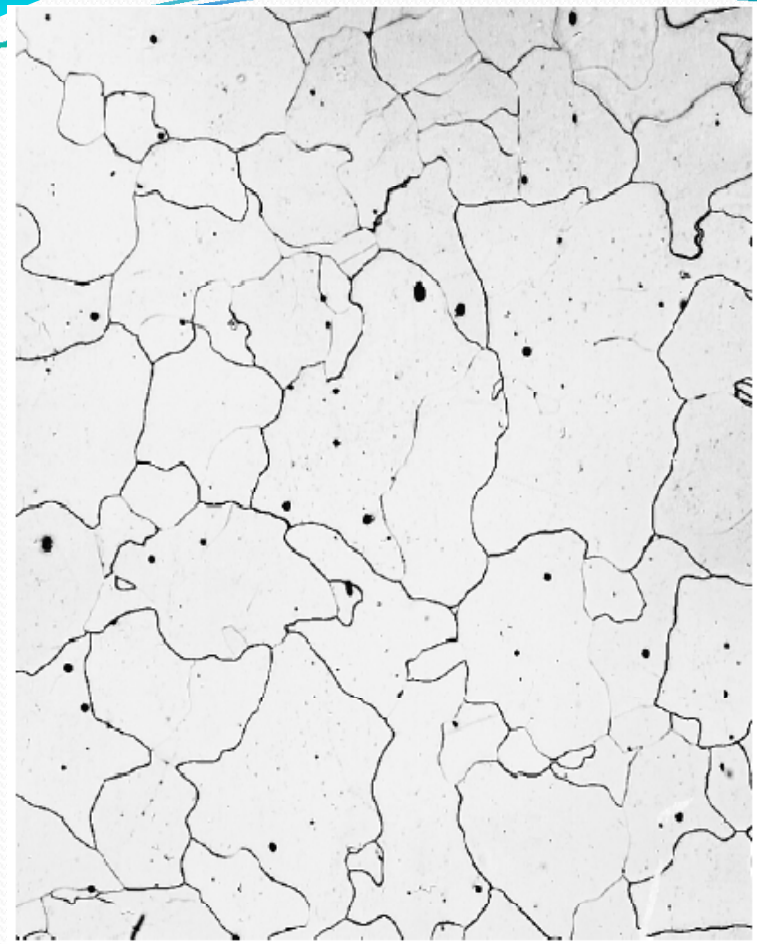
Rail wheel
rail axle
rails

High C steel
0.8-1.4 wt% C

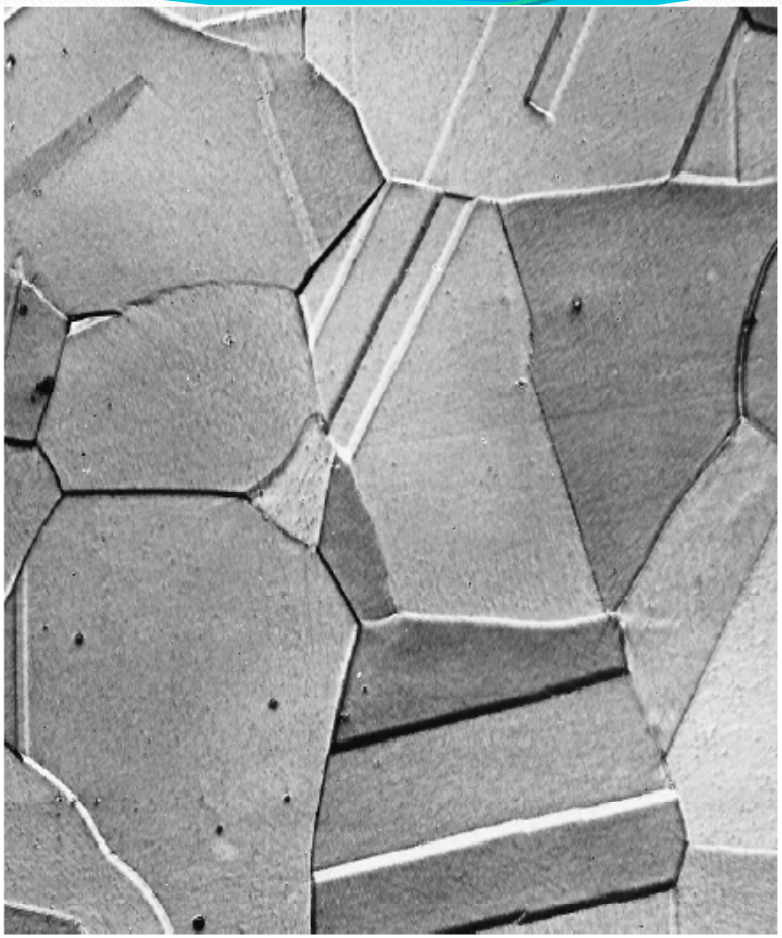
Razor blades
scissors, knives

# 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

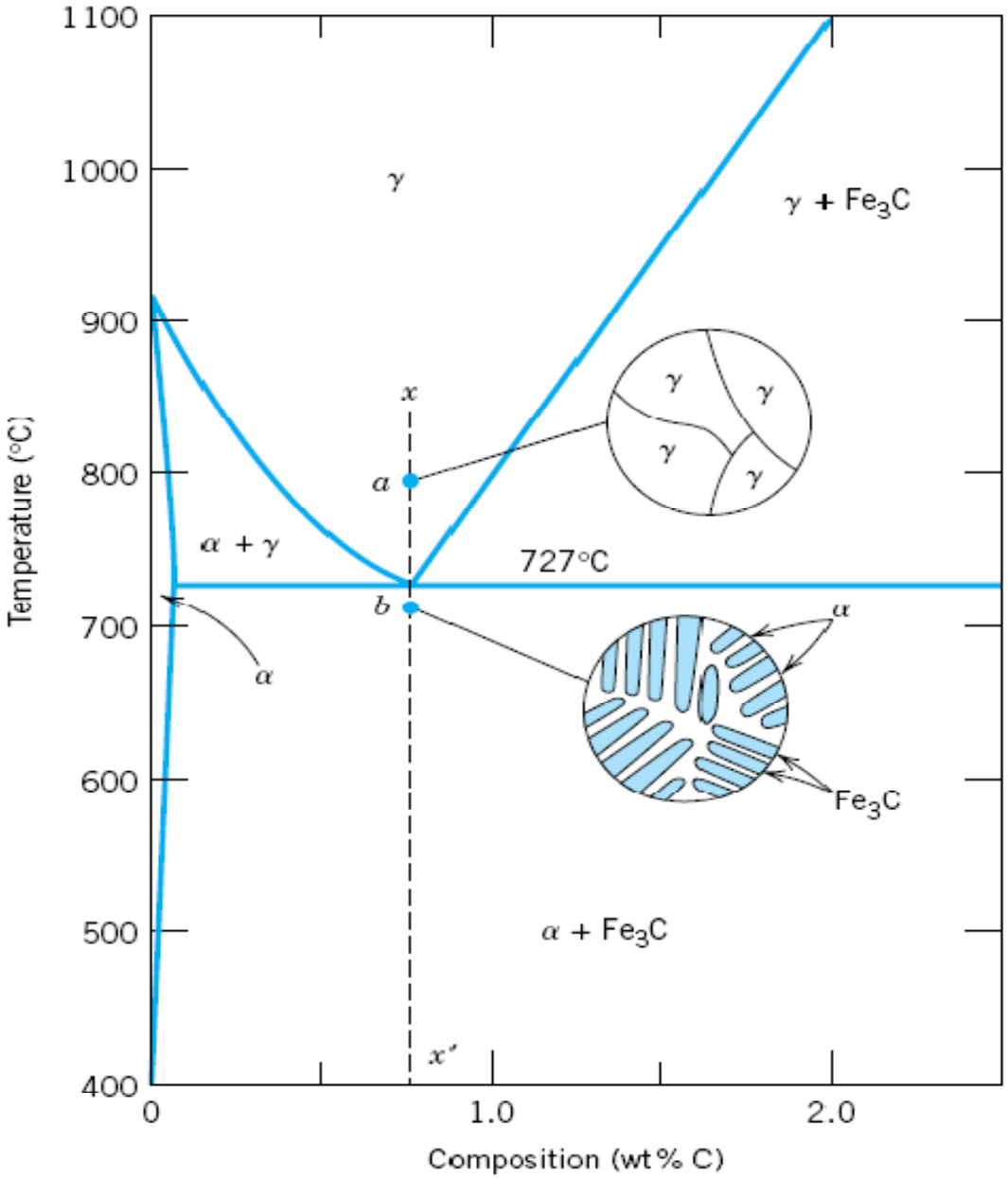
$$\alpha\ (0.1\ wt\%\ C) + L\ (0.5\ wt\%\ C) \xrightarrow{1493^{o}C} \delta\ (0.18\ wt\%\ C)$$

## Eutectic Reaction

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

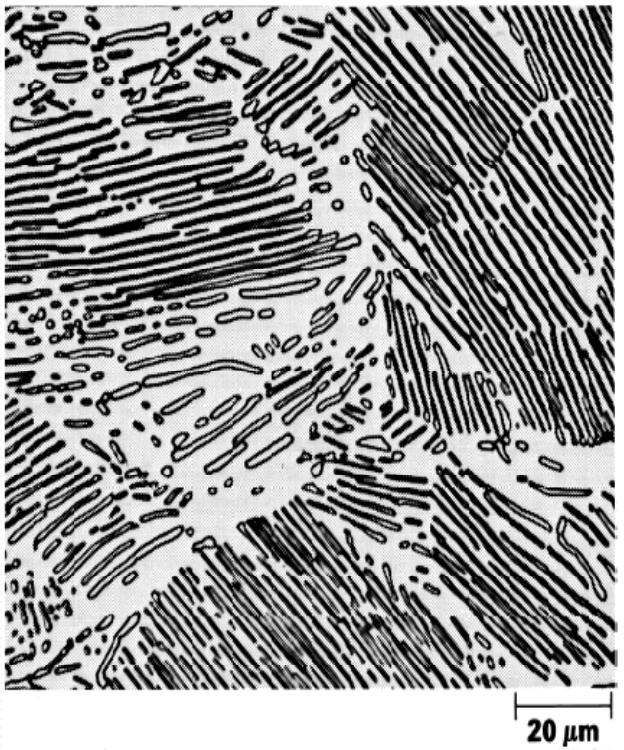
## Eutectoid Reaction

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

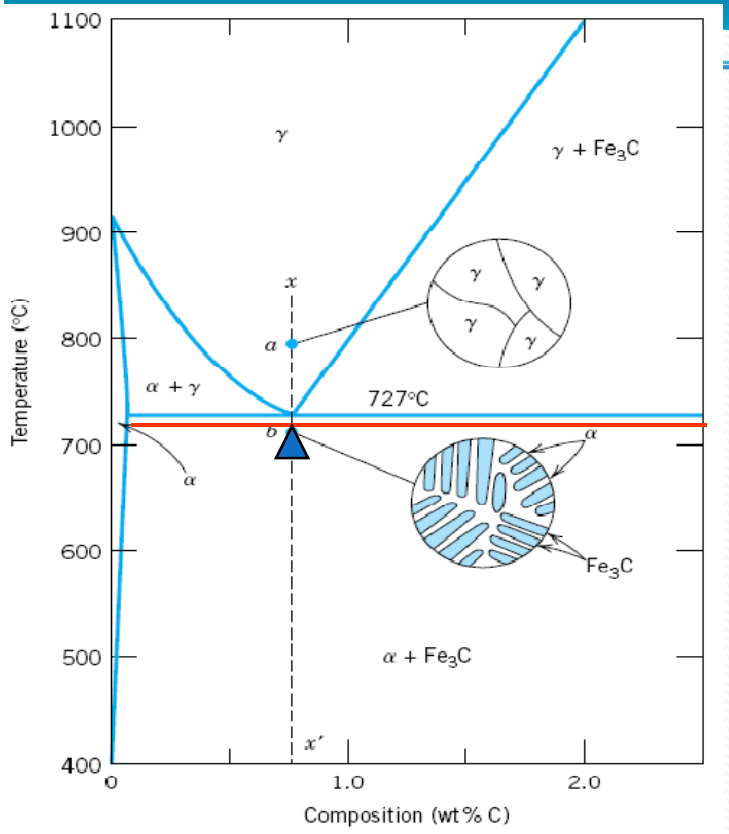



## Eutectoid Reaction

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

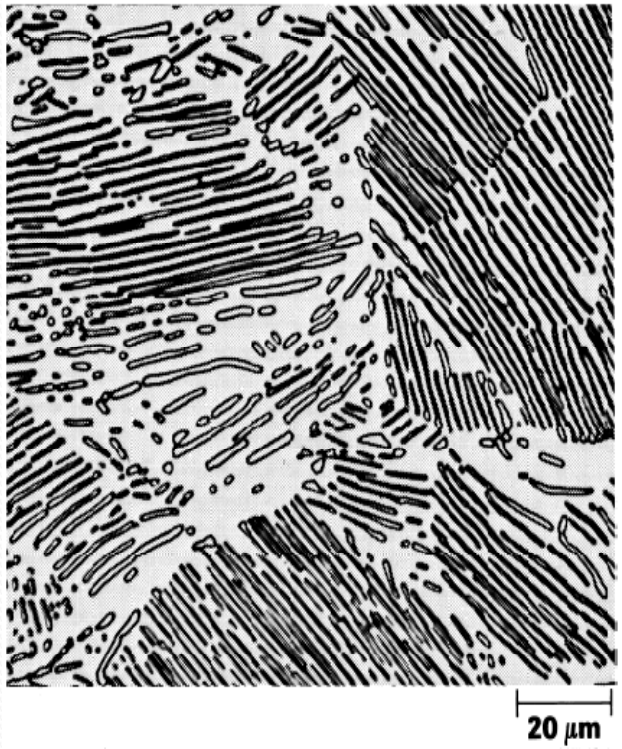


# Eutectoid Reaction




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

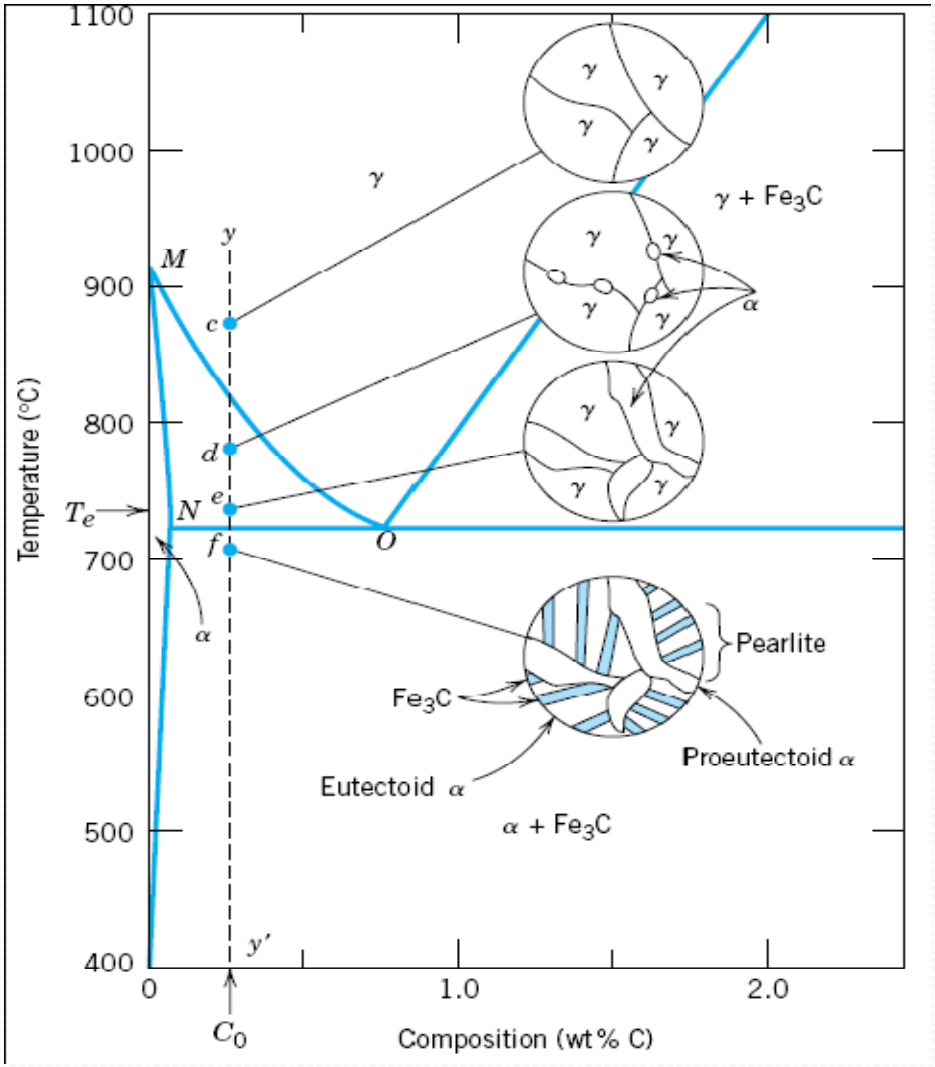
0.8 — 0.02 — 6.67




## Ammount of $Fe_3C$ in Pearlite

## Red Tie Line below eutectoid temp

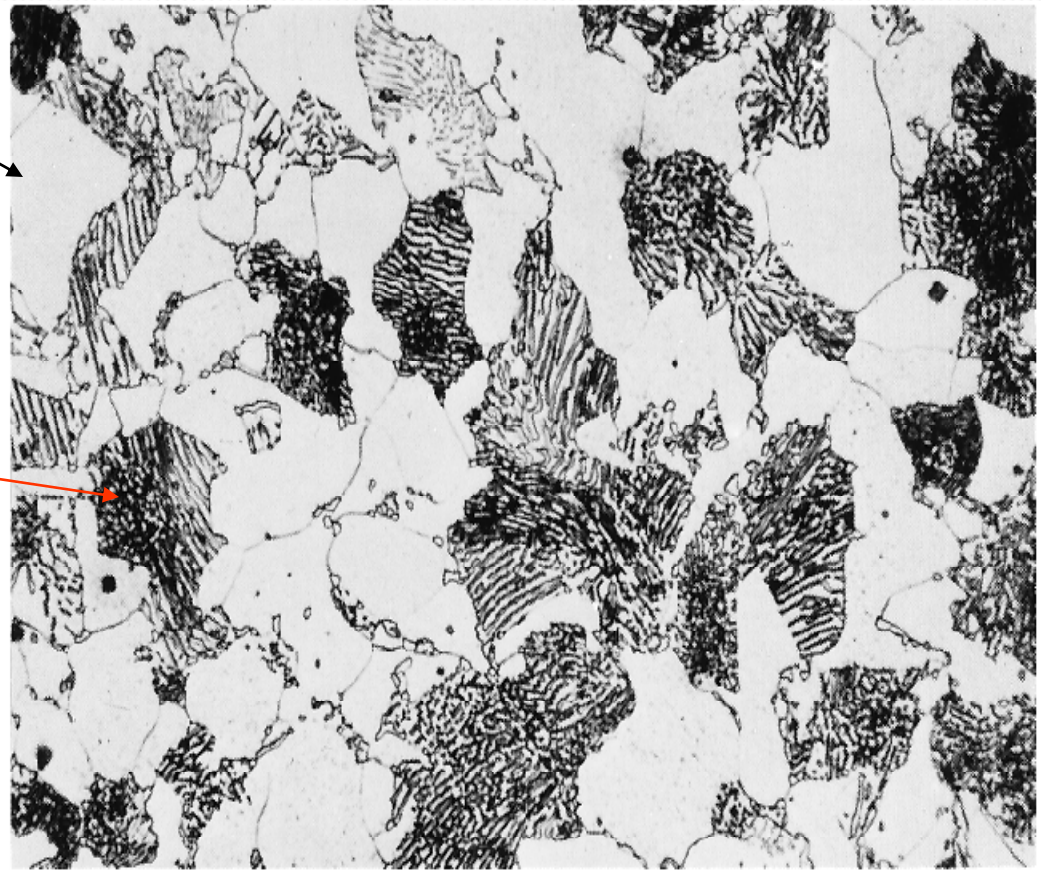
$$f_{F_3C}^{pearlite} = \frac{0.8 - 0.02}{6.67 - 0.02} = \frac{0.78}{6.65} = 0.117$$



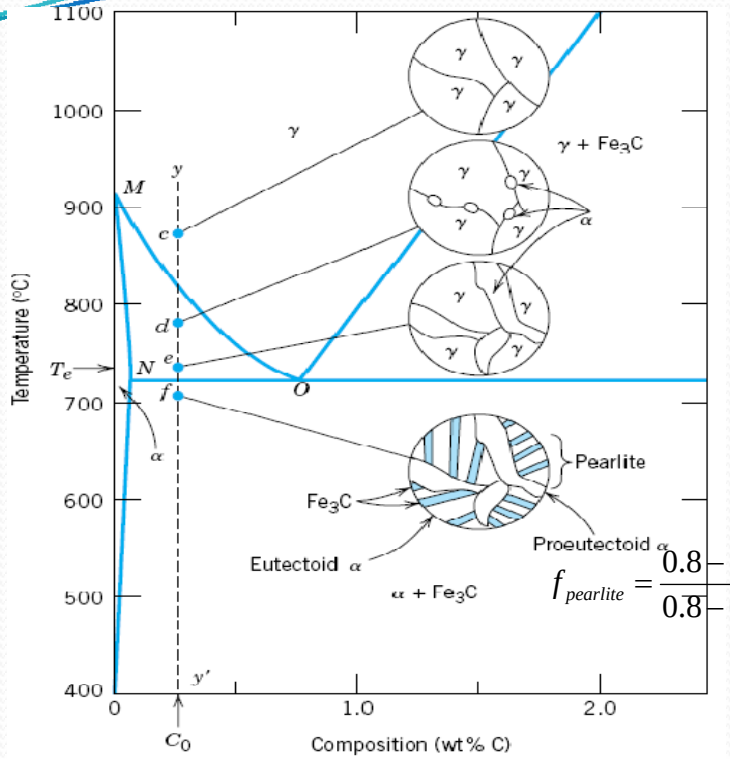

# Development of Microstructure in a hypoeutectoid steel

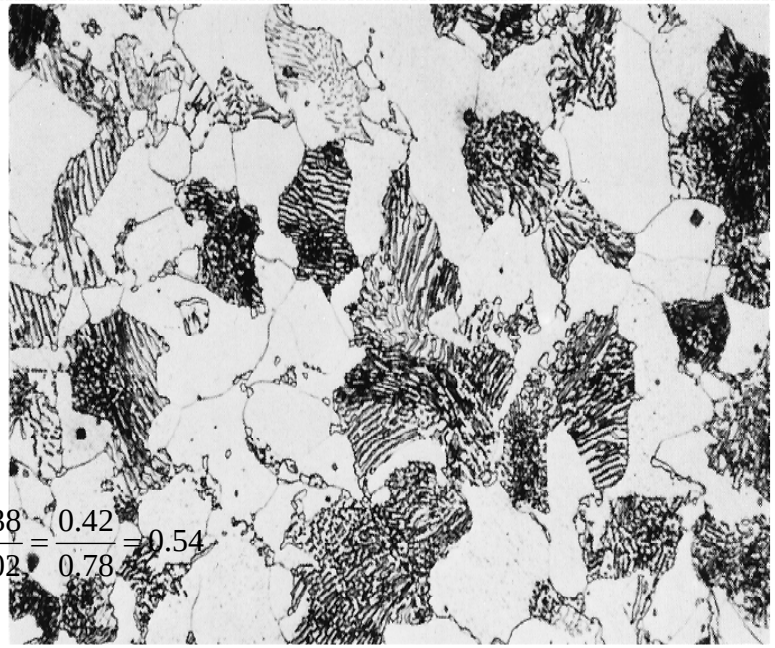
Proeutectoid Ferrite

Pearlite



Microsructure of a hypoeutectoid steel, 0.38 wt% C



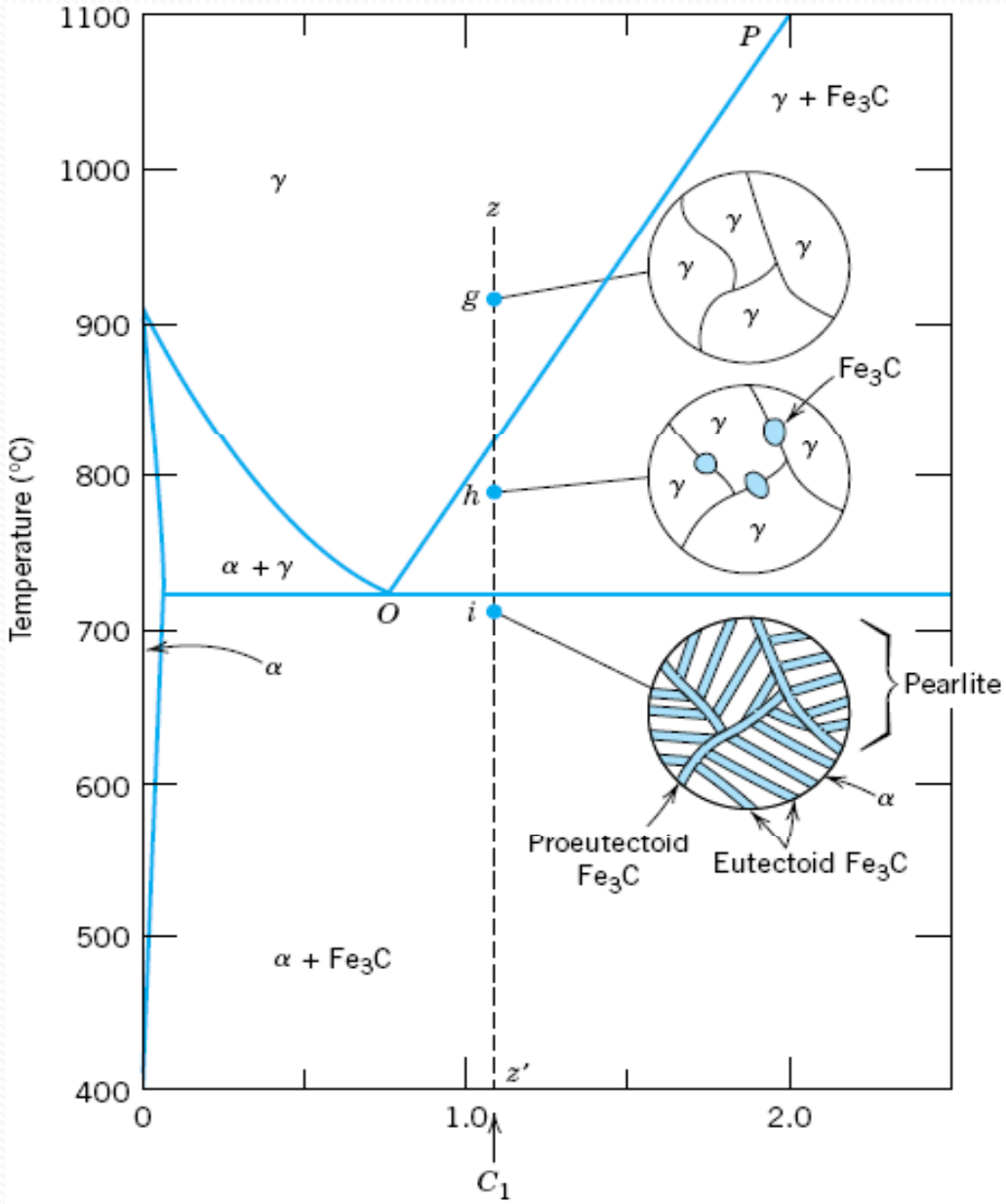



$$f_{pearlite} = \frac{0.8-0.38}{0.8-0.02} = \frac{0.42}{0.78} = 0.54$$

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

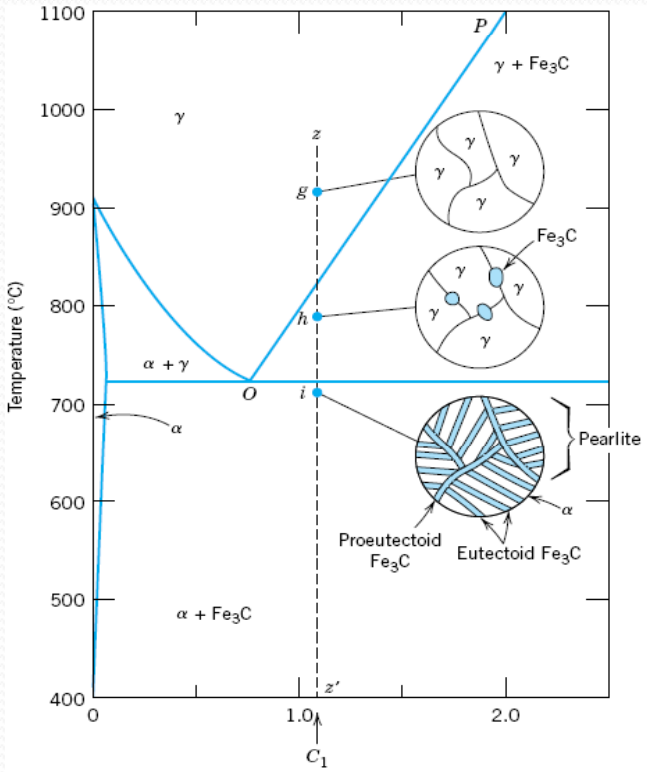
Tie-Line above the eutectoid temperature $T_E$

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




# Development of Microstructure in a hypereutectoid steel


Microsructure of a hypereutectoid steel, 1.4 wt% C




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

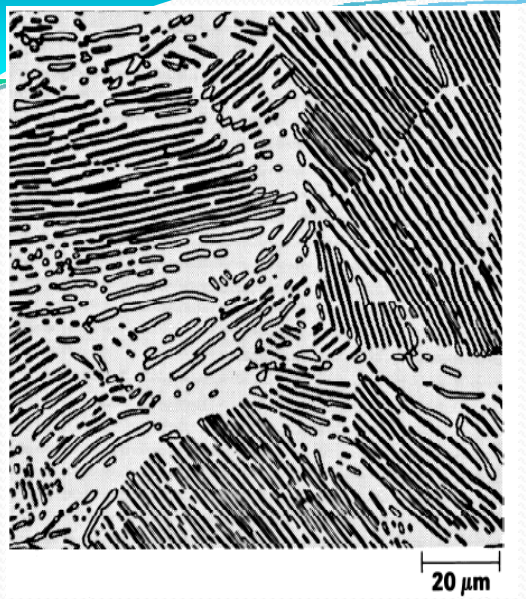
$$f_{proeutectoid\ cementite} = \frac{1.4 - 0.8}{6.67 - 0.8} = \frac{0.6}{5.87} = 0.10$$

# 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 $\alpha$ and $Fe_3C$.




**Eutectoid steel**

$\alpha + Fe_3C$

Pearlite

**Hypoutectoid steel**

$\alpha + Fe_3C$

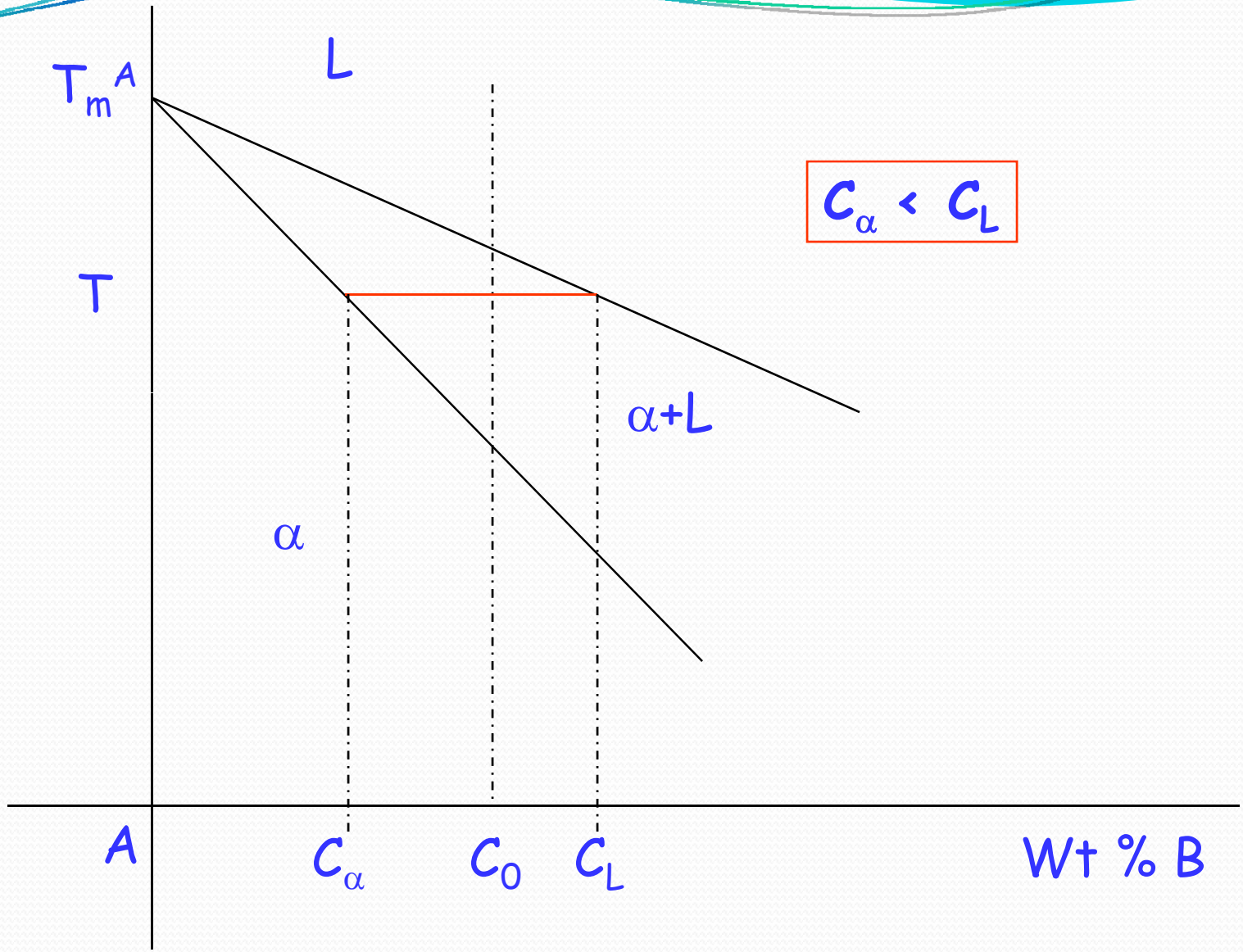
Pearlite + proeutectoid ferrite

**Hypereutectoid steel**

$\alpha + Fe_3C$

Pearlite + proeutectoid cementite

# Principle of Zone Refining



SemiconductorTransistor was invented by

Bardeen, Brattain and Shockley

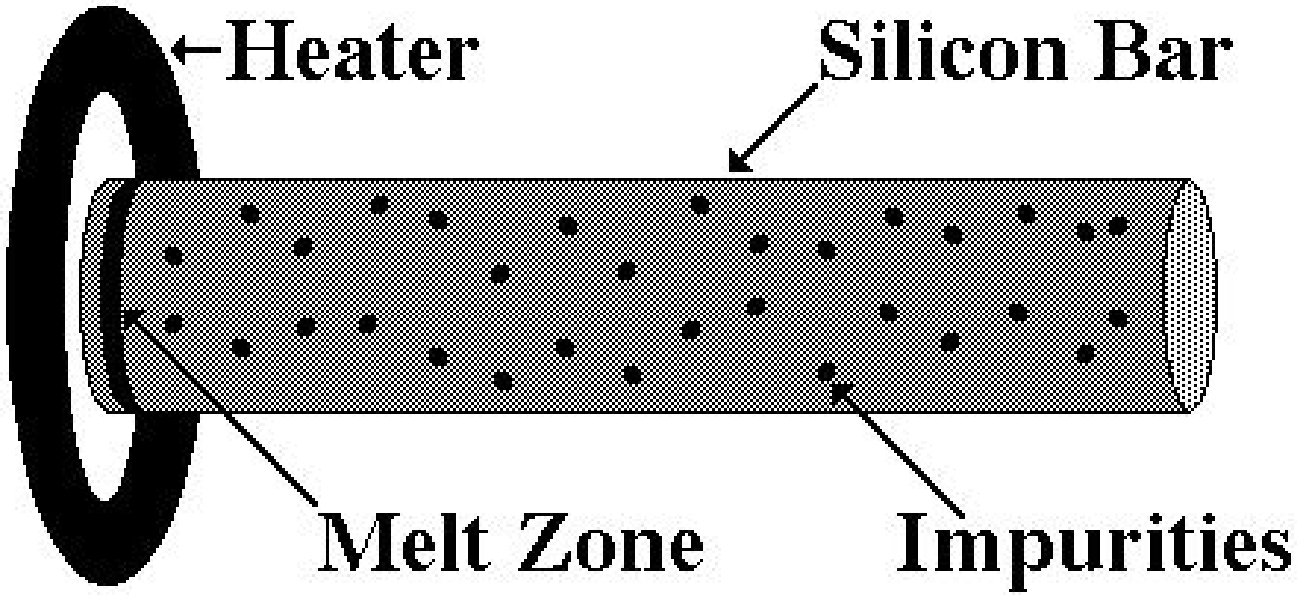
At AT&T Bell Labs

One needs ultrapure Si (impurity level  few ppm)

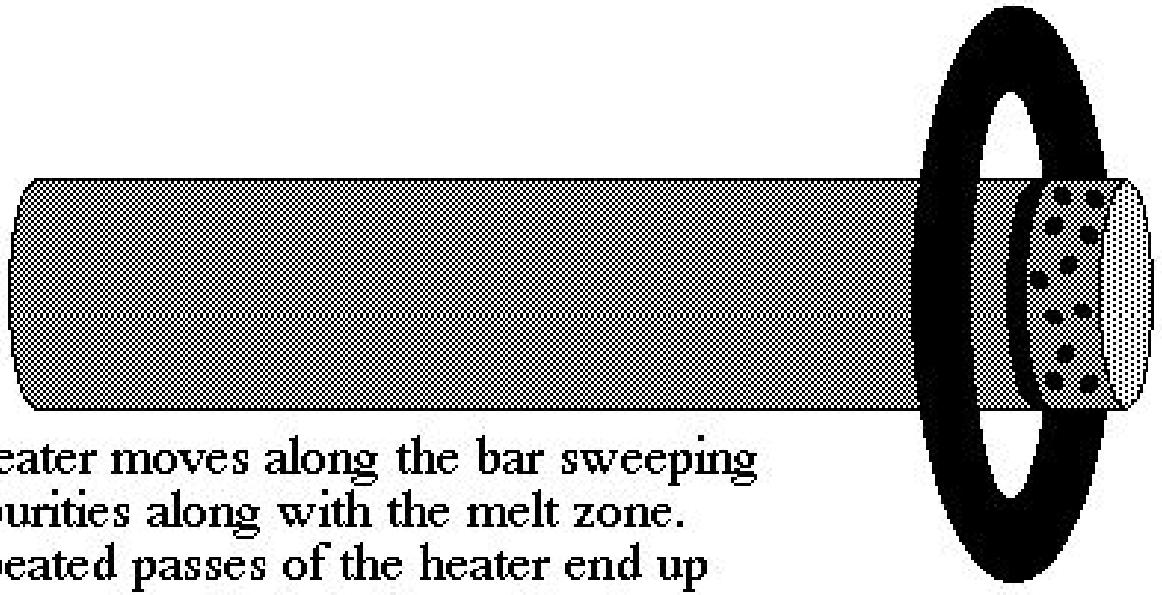
Zone Refining was invented by Pfann at Bell Labs as a process to obtain ultrapure Si

Basis for modern Si technology

# Zone-Refining



# 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.