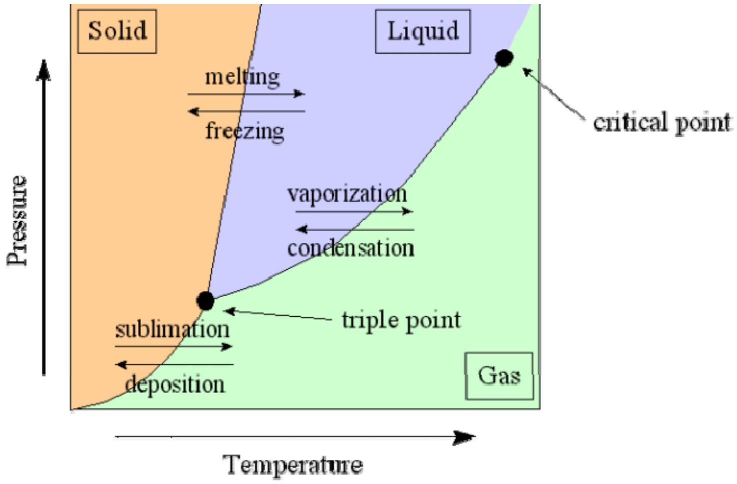
Phase Diagrams

Multiple variables can be plotted:

Chemists are used to Pressure vs. Temperature.

Metallurgists: Temperature vs. Binary Composition,

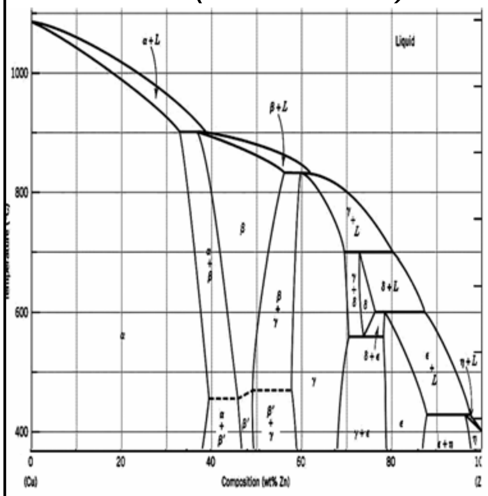
Nobody: Pressure vs. Binary Composition



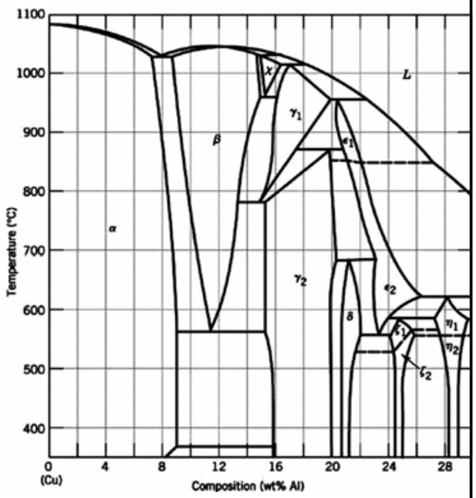
Phase Diagrams

(don't panic)

Cu-Zn (Brass/Bronze)



Al-Cu

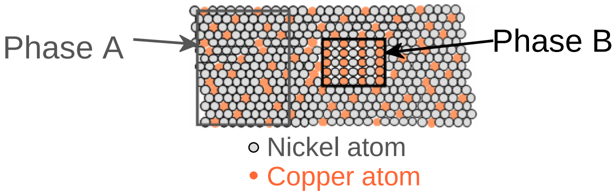


Phase Diagrams

nice tutorial: http://www.soton.ac.uk/~pasr1/

ISSUES TO ADDRESS...

- When we combine two elements...
  what **equilibrium** state do we get?
- In particular, if we specify...
  a composition (e.g., wt% Cu - wt% Ni), and
  a temperature (*T*)
  then...
  How many phases do we get?
  What is the composition of each phase?
  How much of each phase do we get?



Phase Diagrams

For a phase diagram with temperature on the vertical axis, a **solidus** is a line below which the substance is **stable in the solid state.**

A **liquidus** is a line above which the substance is **stable in a liquid state.**

There may be a gap between the solidus and liquidus; within the gap, the substance is in equilibrium only with solid and liquid both present.

The **triple point** of a substance is the temperature and pressure at which three phases (gas, liquid, and solid) of that substance can coexist.

Solid Solutions

A **solid solution** is a solid-state solution of one or more solutes in a solvent.

Solid Solution and **not** a compound **IFF**
crystal structure of remains unchanged by addition
of the solutes **and** the mixture remains
in a single homogeneous phase.

Solute incorporation either *substitutionally or interstitially*

Solid solutions may form if the solute and solvent have:

Similar atomic radii (15% or less difference)
Same crystal structure
Similar electronegativities
Similar coordination number (a.k.a. valency)

Eutectics

eutectic: the composition of a mixture that has the lowest melting point where the phases simultaneously crystallize from molten solution at this temperature.

From the Greek 'eutektos', meaning ‘easily melted’.

When a non-eutectic alloy freezes, one component of the alloy crystallizes at one T and the other at a different T.

With a eutectic alloy, the **mixture freezes as one at a single T.**

A eutectic alloy therefore has a sharp melting point, and a non-eutectic alloy exhibits a plastic melting range.

Uses of Eutectic Phases

soldering: Sn and Pb and sometimes Ag or Au.

casting alloys: Al-Si, cast iron (austenite-cementite Fe-C)

brazing: diffusion removes alloying elements from the joint.

temp. response: Wood's (Bi-Pb-Sn-Cd, mp 70 C) &
Field's (Bi-In-Sn, mp 62 C) metals
for fire sprinklers, prototype casting, repairs

non-toxic mercury replacements: galinstan (Ga-In-Sn)

NaK alloys: liquid at room temperature, used as coolant in
fast neutron nuclear reactors.

Phase Equilibria: Solubility Limit

Introduction

- Solutions – solid solutions, single phase
- Mixtures – more than one phase

- Solubility Limit:
  Max concentration for which only a single phase solution occurs.

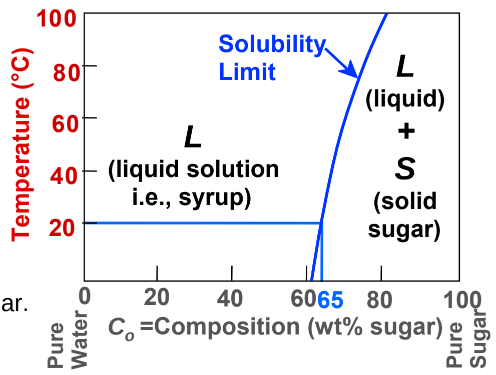
Question: What is the solubility limit at 20°C?

Answer: 65 wt% sugar.

If C_o < 65 wt% sugar: syrup

If C_o > 65 wt% sugar: syrup + sugar.

Sucrose/Water Phase Diagram



Components and Phases

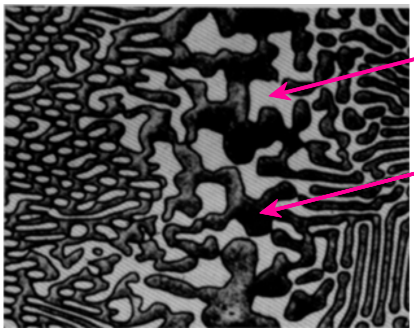
- Components:

  The elements or compounds which are present in the mixture (e.g., Al and Cu)

- Phases:

  The physically and chemically distinct material regions that result (e.g., α and β).

Aluminum-
Copper
Alloy



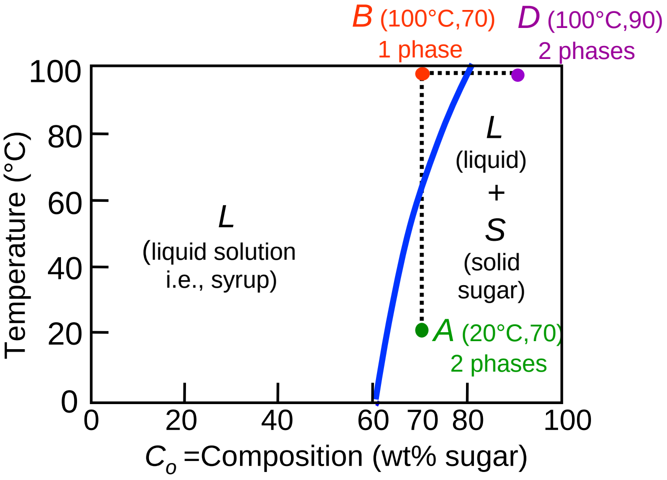
β (lighter phase)

α (darker phase)

Effect of *T* & Composition (C_o)

- Changing *T* can change # of phases: path *A* to *B*.
- Changing C_o can change # of phases: path *B* to *D*.

water-
sugar
system



Adapted from
Fig. 9.1,
Callister 7e.

Phase Equilibria

Simple solution system (e.g., Ni-Cu solution)

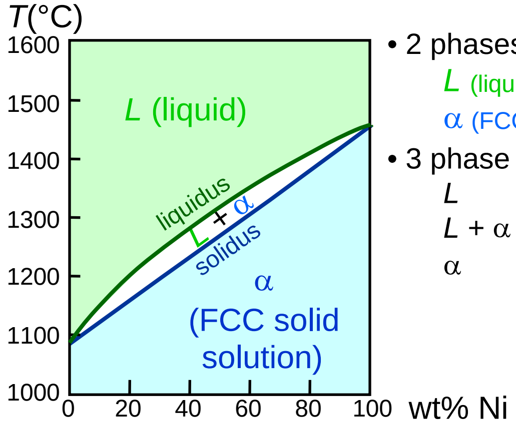
	Crystal Structure	electroneg	*r* (nm)
Ni	FCC	1.9	0.1246
Cu	FCC	1.8	0.1278

- Both have the same crystal structure (FCC) and have similar electronegativities and atomic radii (W. Hume – Rothery rules) suggesting high mutual solubility.
- Ni and Cu are totally miscible in all proportions.

Phase Diagrams

- Indicate phases as function of *T*, C_o, and *P*.
- For this course:
  - -binary systems: just 2 components.
  - -independent variables: *T* and C_o (*P* = 1 atm is almost always used).

- Phase Diagram for Cu-Ni system



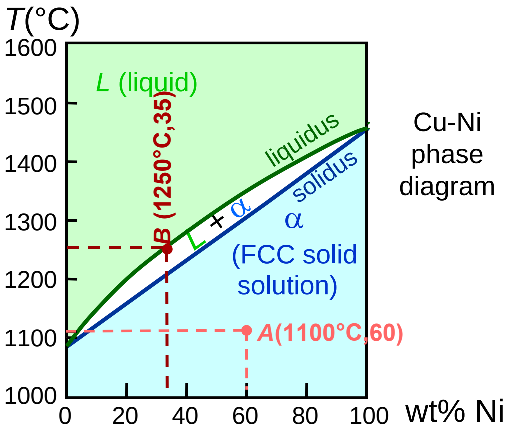
- 2 phases:
  - *L* (liquid)
  - α (FCC solid solution)
- 3 phase fields:
  - *L*
  - *L* + α
  - α

Phase Diagrams:
and types of phases

- Rule 1: **If we know *T* and C_o, then we know the # and types of phases present.**
  - Examples:

A(1100°C, 60):
1 phase: α

B(1250°C, 35):
2 phases: *L* + α



Phase Diagrams:
composition of phases

- Rule 2: **If we know *T* and C_o, then we know the composition of each phase.**
  - Examples:

C_o = 35 wt% Ni

At T_A = 1320°C:

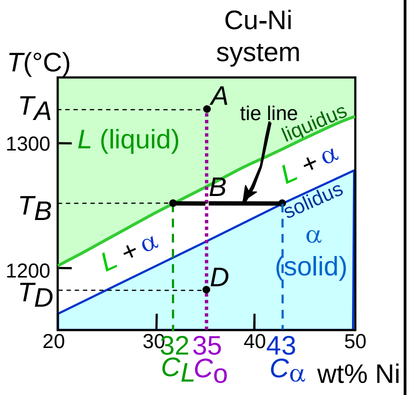
Only Liquid (*L*)
$C_L = C_o$ (= 35 wt% Ni)

At T_D = 1190°C:

Only Solid (α)
$C_\alpha = C_o$ (= 35 wt% Ni)

At T_B = 1250°C:

Both α and *L*
$C_L = C_{\text{liquidus}}$ (= 32 wt% Ni here)
$C_\alpha = C_{\text{solidus}}$ (= 43 wt% Ni here)



Phase Diagrams:
weight fractions of phases

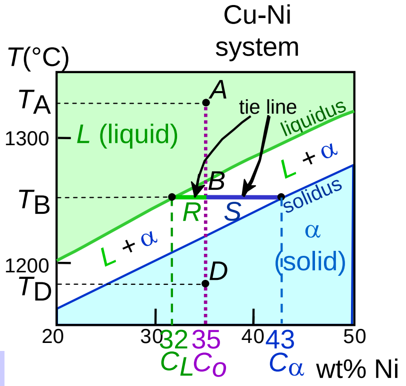
- Rule 3: **If we know *T* and C_o, then we know the amount of each phase (in wt%).**
  - Examples:

C_o = 35 wt% Ni

At T_A: Only Liquid (L)
W_L = 100 wt%, W_α = 0

At T_D: Only Solid (α)
W_L = 0, W_α = 100 wt%

At T_B: Both α and *L*

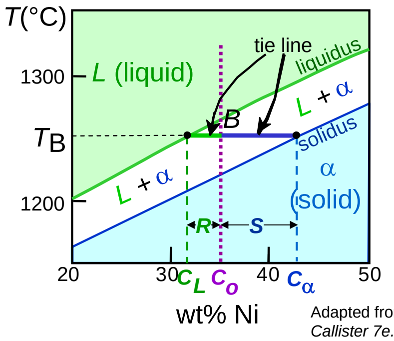


$$\boxed{W_L = \frac{S}{R+S}} = \frac{43-35}{43-32} = 73\,wt\%$$

$$\boxed{W_\alpha = \frac{R}{R+S}} = 27\text{ wt\%}$$

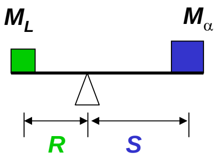
The Lever Rule

- Tie line – connects the phases in equilibrium with each other: i.e., essentially an iso“therm”



Adapted from Fig. 9.3(b), *Callister 7e.*

How much of each phase?
Think of it as a lever (teeter-totter)



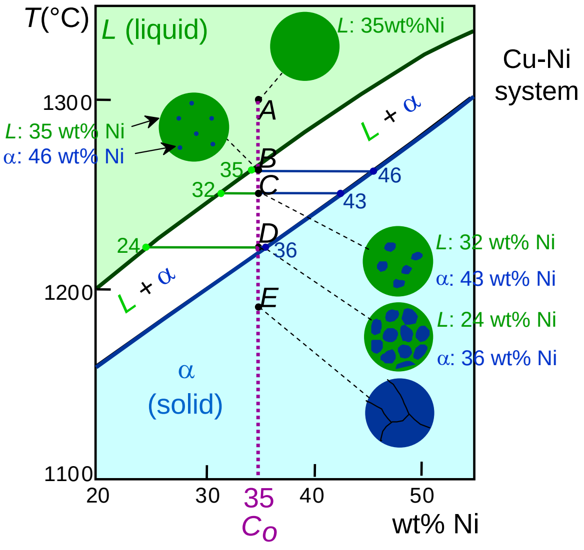
$$M_\alpha \cdot S = M_L \cdot R$$

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

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

Ex: Cooling in a Cu-Ni Binary

- Phase diagram:
  Cu-Ni system.
- System is:
  binary
  i.e., 2 components:
  Cu and Ni.
  isomorphous
  i.e., complete
  solubility of one
  component in
  another; α phase
  field extends from
  0 to 100 wt% Ni.
- Consider
  C_o = 35 wt%Ni.



Frustration during Crystallization

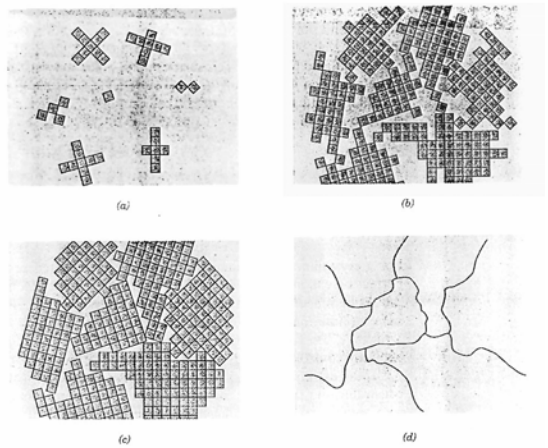
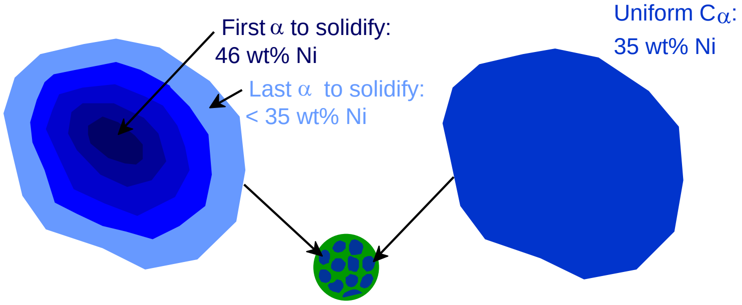


FIGURE 3.16 Schematic diagrams of the various stages in the solidification of a polycrystalline material; the square grids depict unit cells. (*a*) Small crystallite nuclei. (*b*) Growth of the crystallites; the obstruction of some grains that are adjacent to one another is also shown. (*c*) Upon completion of solidification, grains having irregular shapes have formed. (*d*) The grain structure as it would appear under the microscope; dark lines are the grain boundaries. (Adapted from W. Rosenhain, *An Introduction to the Study of Physical Metallurgy*, 2nd edition, Constable & Company Ltd., London, 1915.)

Compositional Non-Equilibrium Phases

- C_{α} changes as we solidify.
- Cu-Ni case: First α to solidify has C_{α} = 46 wt% Ni.
  Last α to solidify has C_{α} = 35 wt% Ni.

- Fast rate of cooling:
  Cored structure
- Slow rate of cooling:
  Equilibrium structure



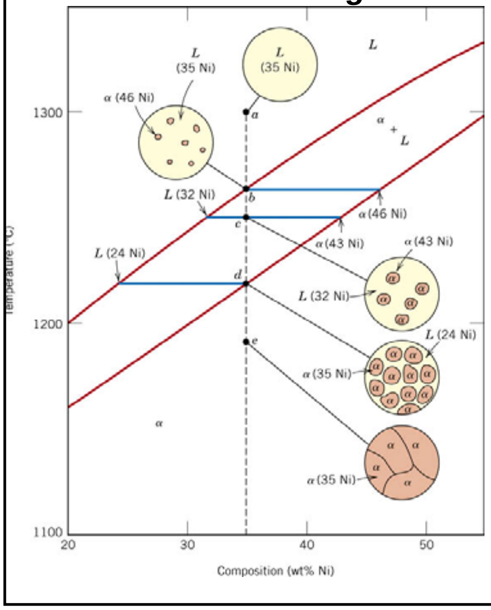
First α to solidify:
46 wt% Ni

Last α to solidify:
< 35 wt% Ni

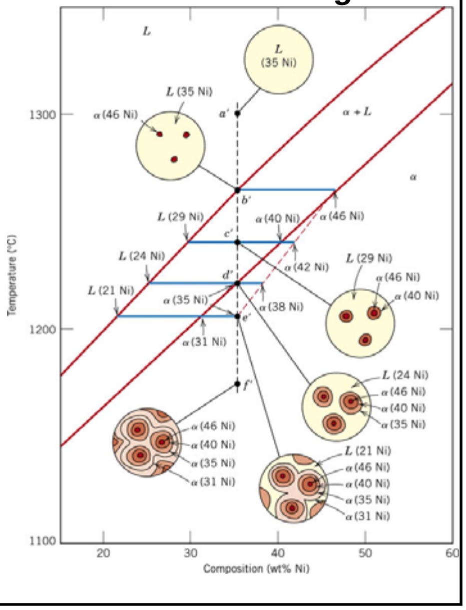
Uniform C_{α}:
35 wt% Ni

Equilibrium vs. Cored Phases

slow cooling



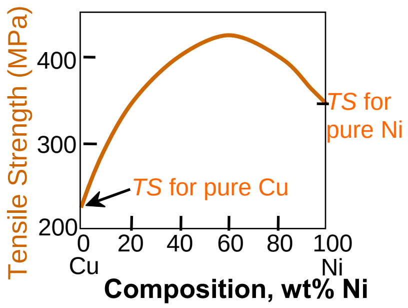
fast cooling



Mechanical Properties: Cu-Ni System

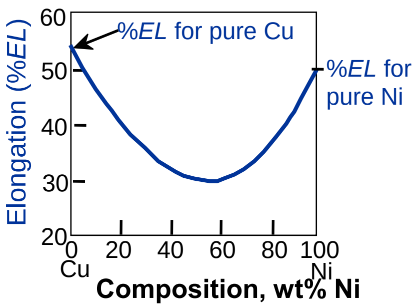
- Effect of solid solution strengthening on:

Tensile strength (*TS*)



Peak as a function of C_o

Ductility (%*EL*,%*AR*)



Min. as a function of C_o

Binary-Eutectic Systems

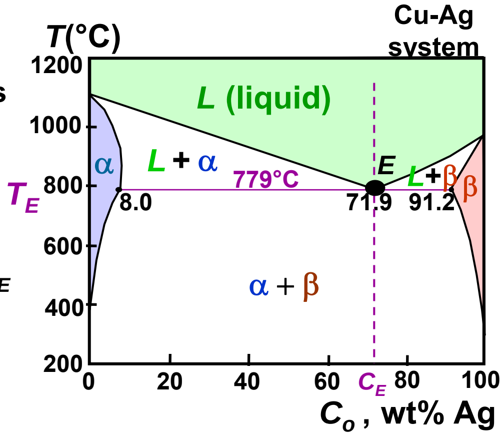
2 components

has a special composition with a min. melting T.

Ex.: Cu-Ag system

- 3 single phase regions (L, α, β)
- Limited solubility:
  - α: mostly Cu
  - β: mostly Ag
- T_E : No liquid below T_E
- C_E : Min. melting T_E composition
- Eutectic transition

$$L(C_E) \rightleftharpoons \alpha(C_{\alpha E}) + \beta(C_{\beta E})$$



Gibbs Phase Rule

F = C + N - P

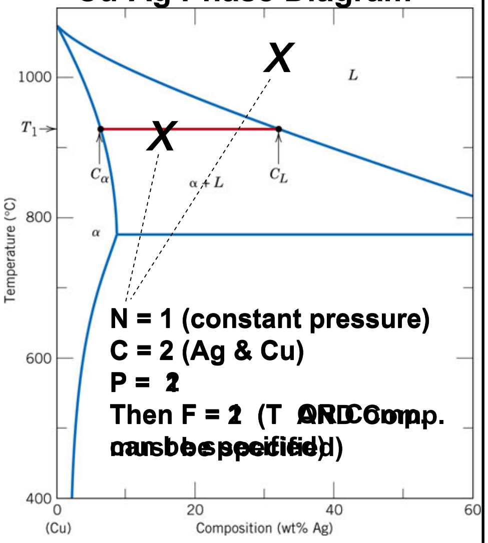
F = degrees of freedom necessary to specify the system (# of ext. variables, e.g., T, P, Comp.)

P = # of phases

C = # of components

N = # of non-compositional variables

Cu-Ag Phase Diagram



N = 1 (constant pressure)
C = 2 (Ag & Cu)
P = 1
Then F = 2 (T AND Comp. can be specified)

N = 1 (constant pressure)
C = 2 (Ag & Cu)
P = 2
Then F = 1 (T OR Comp. must be specified)

At Eutectic
N = 1 (constant pressure)
C = 2 (Ag & Cu)
P = 3
Then F = 0 (no variables)

Pb-Sn Eutectic System (1)

For a 40 wt% Sn-60 wt% Pb alloy at 150°C, find...

- **the phases present:** $\alpha + \beta$
- **compositions of phases:**

  $C_O = 40$ wt% Sn
  $C_\alpha = 11$ wt% Sn
  $C_\beta = 99$ wt% Sn

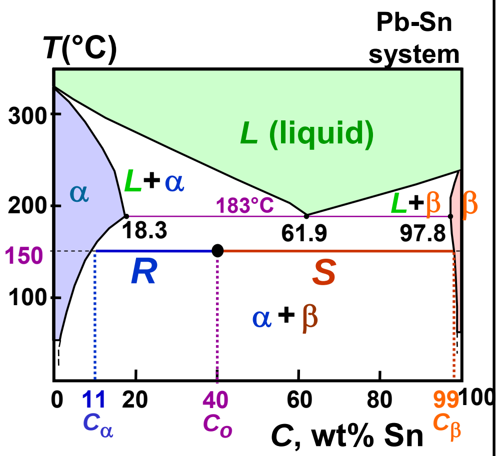
- **the relative amount of each phase:**

$$W_\alpha = \frac{S}{R+S} = \frac{C_\beta - C_O}{C_\beta - C_\alpha}$$

$$= \frac{99 - 40}{99 - 11} = \frac{59}{88} = 67 \text{ wt\%}$$

$$W_\beta = \frac{R}{R+S} = \frac{C_O - C_\alpha}{C_\beta - C_\alpha}$$

$$= \frac{40 - 11}{99 - 11} = \frac{29}{88} = 33 \text{ wt\%}$$



Pb-Sn Eutectic System (2)

For a 40 wt% Sn-60 wt% Pb alloy at 200°C, find...

- **the phases present:** $\alpha + L$
- **compositions of phases:**

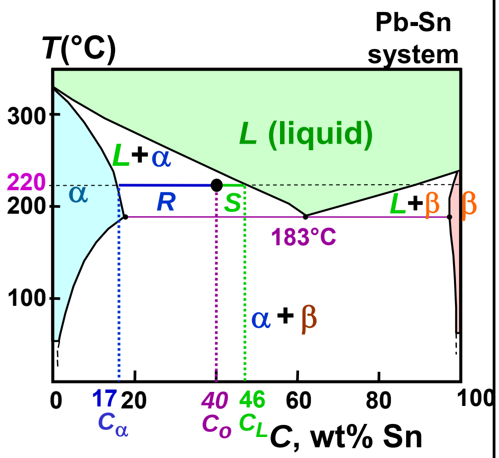
  $C_O = 40$ wt% Sn
  $C_\alpha = 17$ wt% Sn
  $C_L = 46$ wt% Sn

- **the relative amount of each phase:**

$$W_\alpha = \frac{C_L - C_O}{C_L - C_\alpha} = \frac{46 - 40}{46 - 17}$$

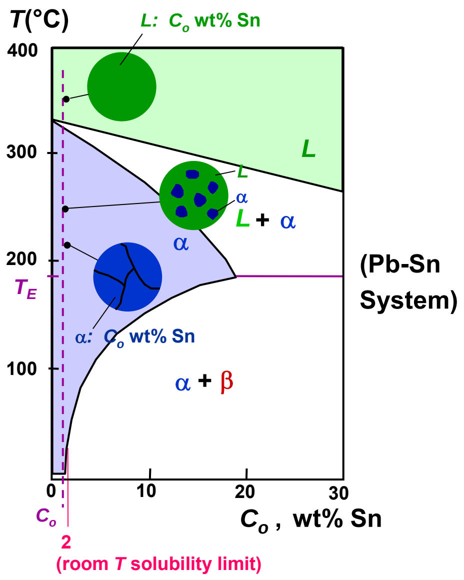
$$= \frac{6}{29} = 21 \text{ wt\%}$$

$$W_L = \frac{C_O - C_\alpha}{C_L - C_\alpha} = \frac{23}{29} = 79 \text{ wt\%}$$



Microstructures in Eutectic Systems: I

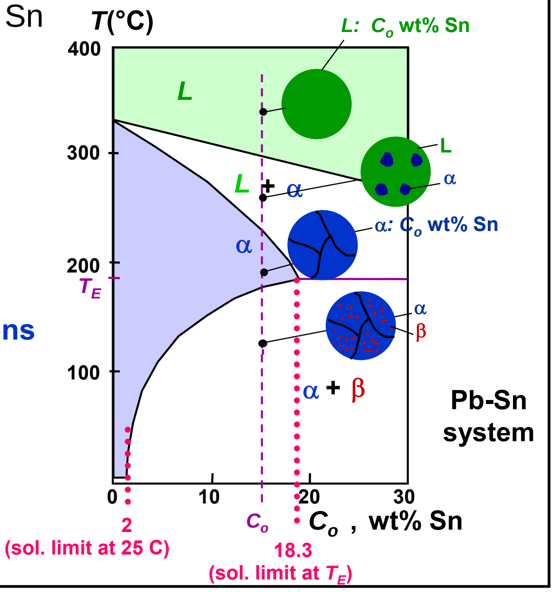
- C_o < 2 wt% Sn
- **Result:**
  polycrystal of α grains only
  i.e., only one solid phase.



(Pb-Sn System)

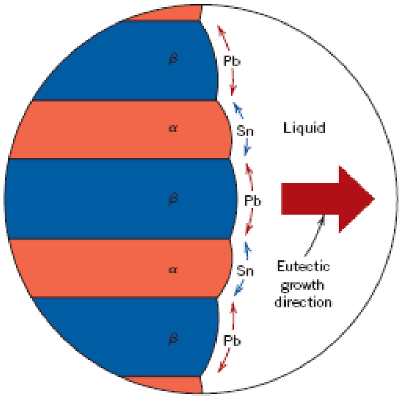
Microstructures in Eutectic Systems: II

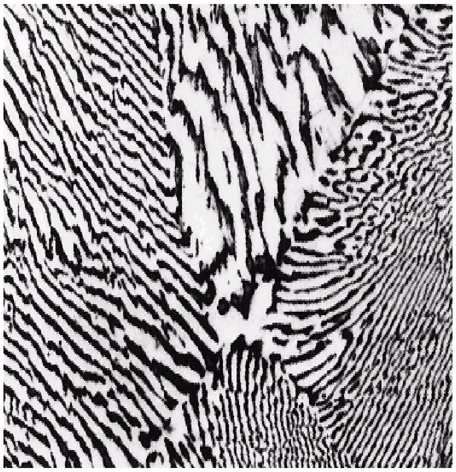
- 2 wt% Sn < C_o < 18.3 wt% Sn
- Result:
  - **Initially liquid + α**
  - **then α alone**
  - **finally two phases**
    - **α polycrystal**
    - **fine β-phase inclusions**



Pb-Sn system

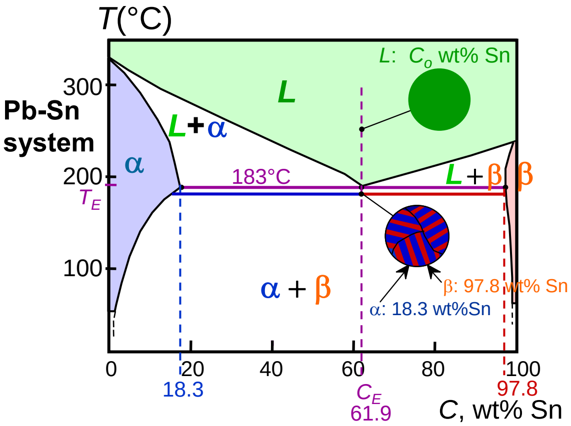
Lamellar Eutectic Structure



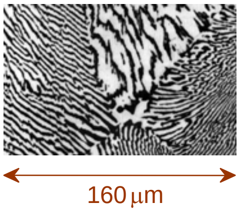


Microstructures in Eutectic Systems: III

- $C_o = C_E$
- **Result: Eutectic microstructure (lamellar structure) alternating layers (lamellae) of α and β crystals.**

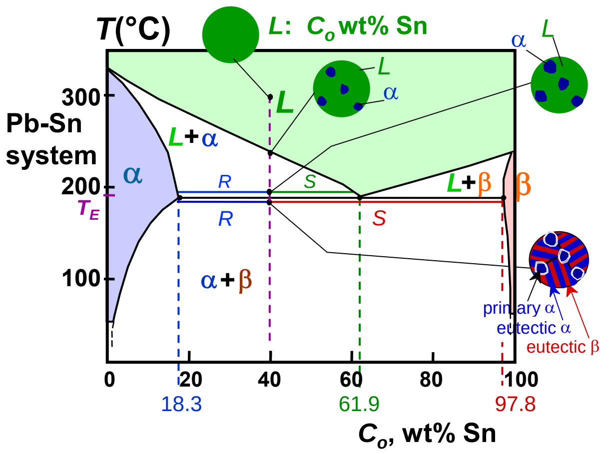


Micrograph of Pb-Sn eutectic microstructure



Microstructures in Eutectic Systems: IV

- 18.3 wt% Sn < C_o < 61.9 wt% Sn
- **Result:** **α crystals and a eutectic microstructure**



- Just above T_E :

C_α = 18.3 wt% Sn

C_L = 61.9 wt% Sn

$W_\alpha = \dfrac{S}{R+S}$ = 50 wt%

W_L = (1- W_α) = 50 wt%

- Just below T_E :

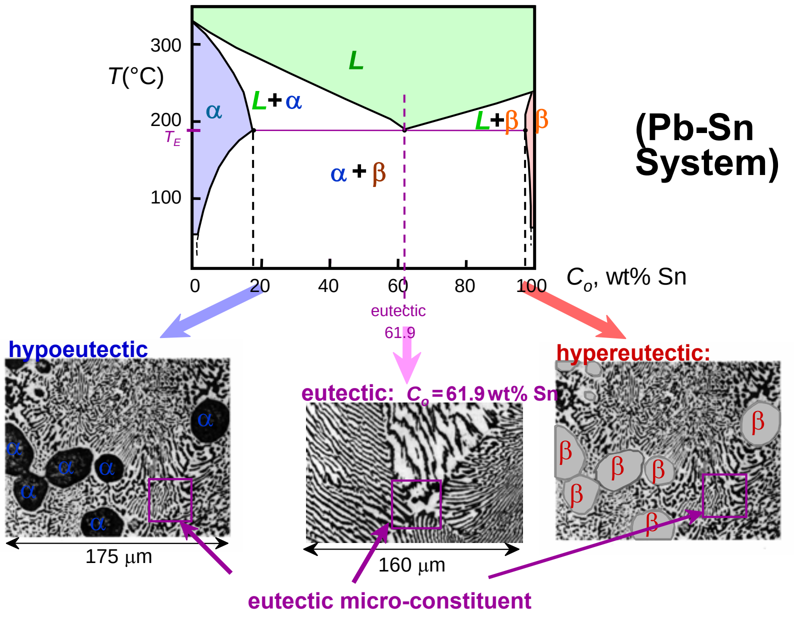
C_α = 18.3 wt% Sn

C_β = 97.8 wt% Sn

$W_\alpha = \dfrac{S}{R+S}$ = 73 wt%

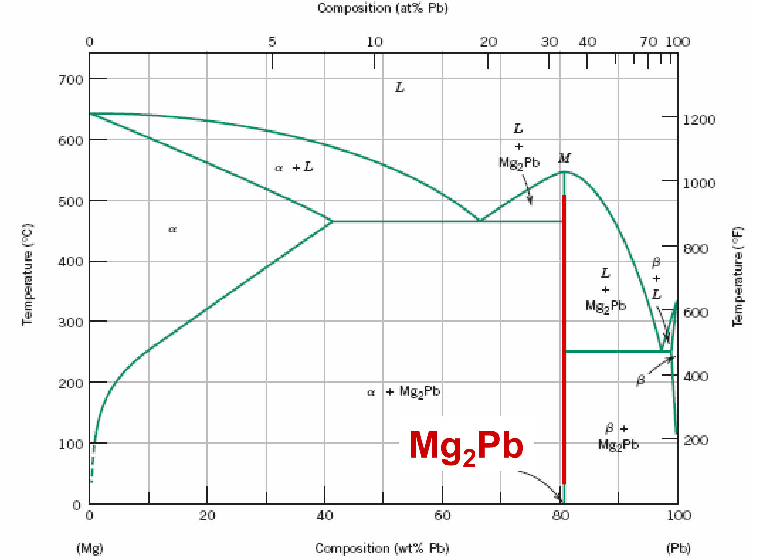
W_β = 27 wt%

Hypoeutectic & Hypereutectic



(Pb-Sn System)

Intermetallic Compounds



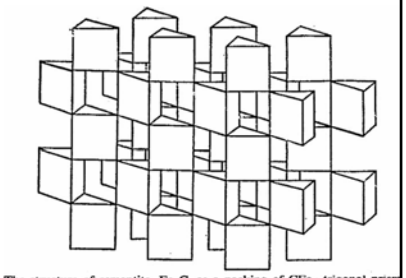
Note: intermetallic compound forms a line - not an area - because stoichiometry (i.e. composition) is exact.

Fe-C Phase Equilibria

Ferrite: **BCC α-Fe Relatively soft and ductile; magnetic at RT.**
Max C solubility 0.022%

Austenite: **FCC γ-Fe Ductile only at elevated temperatures;**
nonmagnetic at high temperatures.
Max C solubility 2.1%

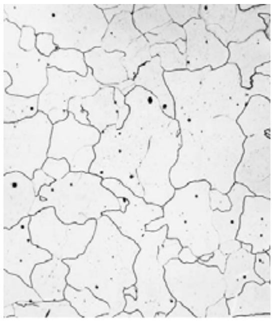
Cementite: **Fe_3C a Compound,**
not an alloy. 6.69% C.



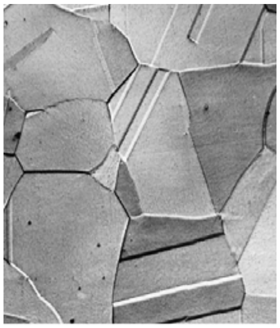
The structure of cementite, Fe_3C, as a packing of CFe_6 trigonal prism

Martensite: **a grain structure not a phase.**
Cystal structure is formed by
displacive transformation
(i.e., unit cell distortion),
not by much slower diffusion.

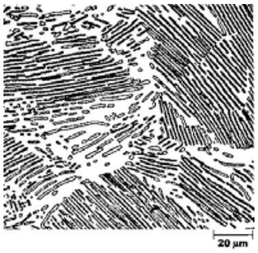
Fe-C Phase Equilibria



Ferrite



Austenite



Pearlite

(cementite+ austentite)

Eutectoid & Peritectic

- **Eutectic:** **liquid in equilibrium with two solids**

$$L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + \beta$$

- **Eutectoid:** **solid phase in equilibrium with 2 solid Phases**

$$S_2 \rightleftharpoons S_1 + S_3$$

intermetallic compound
- cementite

$$\gamma \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \alpha + Fe_3C \qquad (727^oC)$$

- **Peritectic:** **liquid + solid 1 in equilbrium with solid 2**

$$S_1 + L \rightleftharpoons S_2$$

$$\delta + L \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} \gamma \qquad (1493^oC)$$

Eutectoid

Eutectoid Transformation: A solid-solution conversion to a mixture of solids.

e.g., Fe-C: austenite phase can undergo a eutectoid transformation to produce ferrite and cementite (iron carbide), often in lamellar structures such as pearlite and bainite.

This eutectoid point is at about 0.6% carbon; alloys of nearly this composition are called **high-carbon steel**, while those which do not undergo eutectoid transformation are termed **mild steel**.

The process analogous to glass formation in this system is the **martensitic** transformation.

Peritectic

Peritectic Transformation: when a liquid and solid phase of fixed proportions react at a fixed temperature to yield a single solid phase.

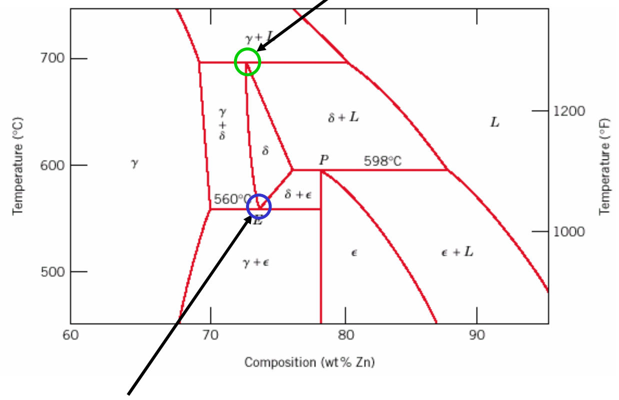
Since the solid product forms at the interface between the two reactants, it can form a diffusion barrier and generally causes such reactions to proceed much more slowly than eutectic or eutectoid transformations.

Because of this, when a peritectic composition solidifies it does not show the lamellar structure (which is typical of eutectic freezing).

Eutectoid & Peritectic

Peritectic transition $\gamma + L \rightleftharpoons \delta$

Cu-Zn Phase diagram



Eutectoid transition $\delta \rightleftharpoons \gamma + \varepsilon$

Fe-C Phase Equilibria

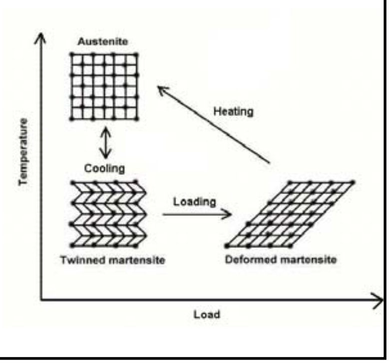
Martensite: a grain structure not truly a phase.

Cystal structures formed by displacive transformation
(i.e., unit cell distortion), not by much slower diffusive transformations.
Often form lenticular (lens-shaped) crystal grains
(which appear needle-shaped in x-section).

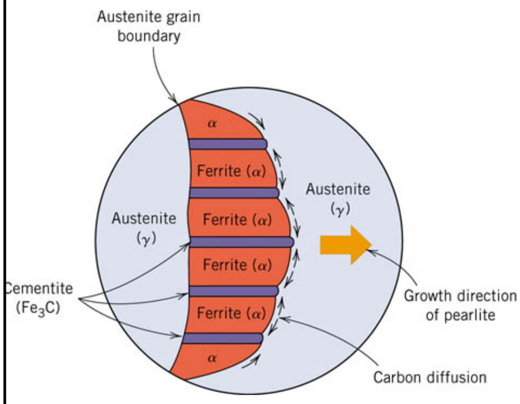
Martensite is specifically a form of ferrite
supersaturated with C => very hard steels
(springs and piano wire).

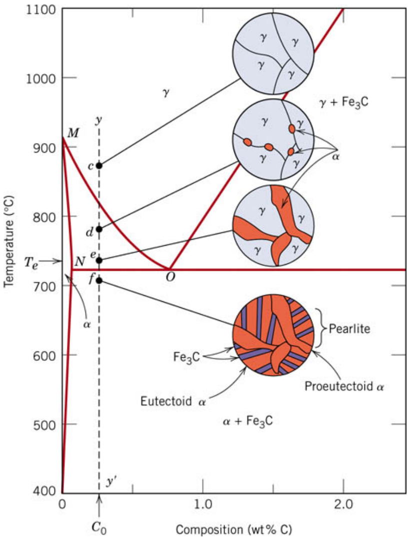
Martensite is formed by rapid cooling
of austenite which traps carbon atoms
that do not have time to diffuse out
of the crystal structure.

Martensite "phases" show memory effects.
http://www.lassp.cornell.edu/sethna/
Tweed/What_Are_Martensites.html



Diffusional Frustration during Crystallization





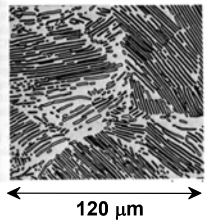
Iron-Carbon (Fe-C) Phase Diagram

Eutectic (*A*):

$L \Rightarrow \gamma + Fe_3C$

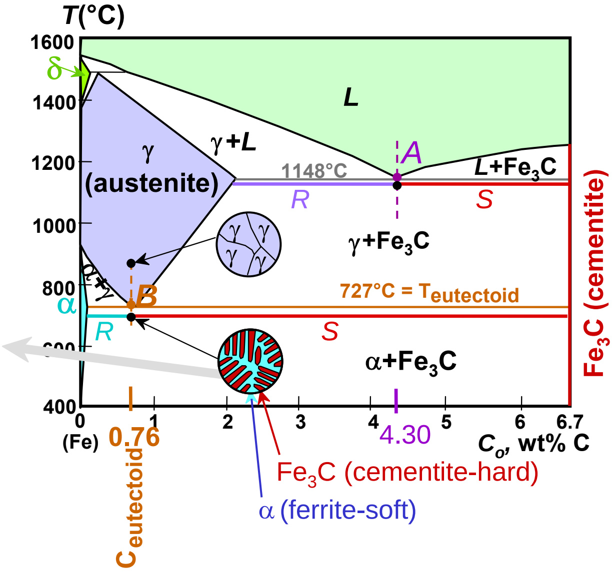
Eutectoid (*B*):

$\gamma \Rightarrow \alpha + Fe_3C$

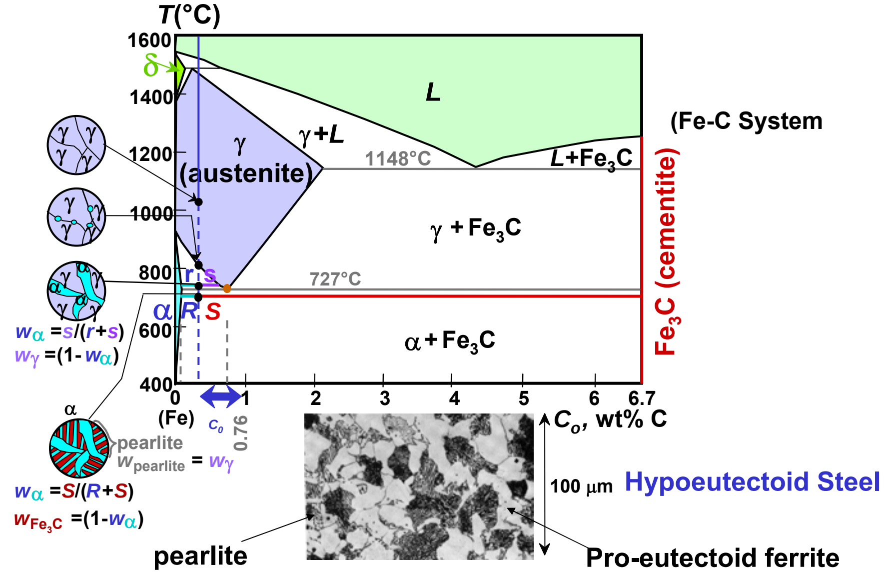


120 μm

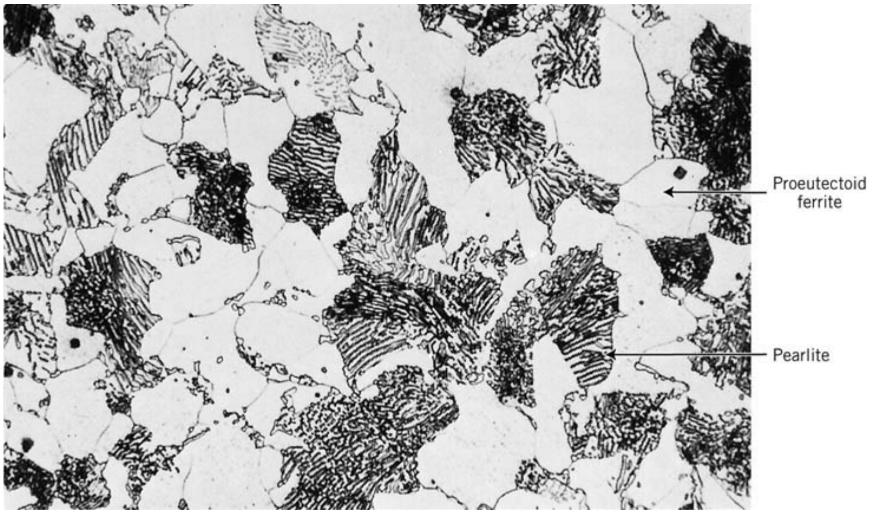
Result: Pearlite = alternating layers of α and Fe$_3$C phases



Hypoeutectoid Steel



Pro-euctectoid: phase that separates out before eutectoid forms



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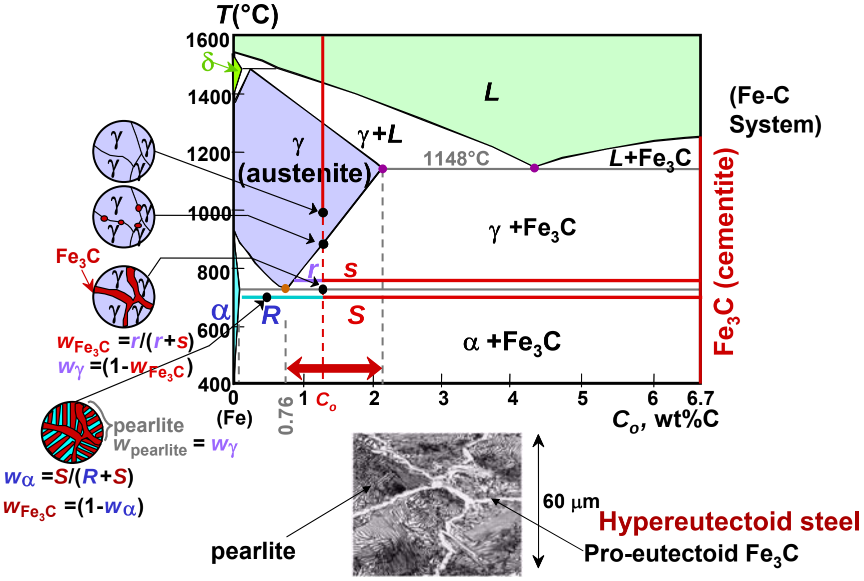
Hypereutectoid Steel



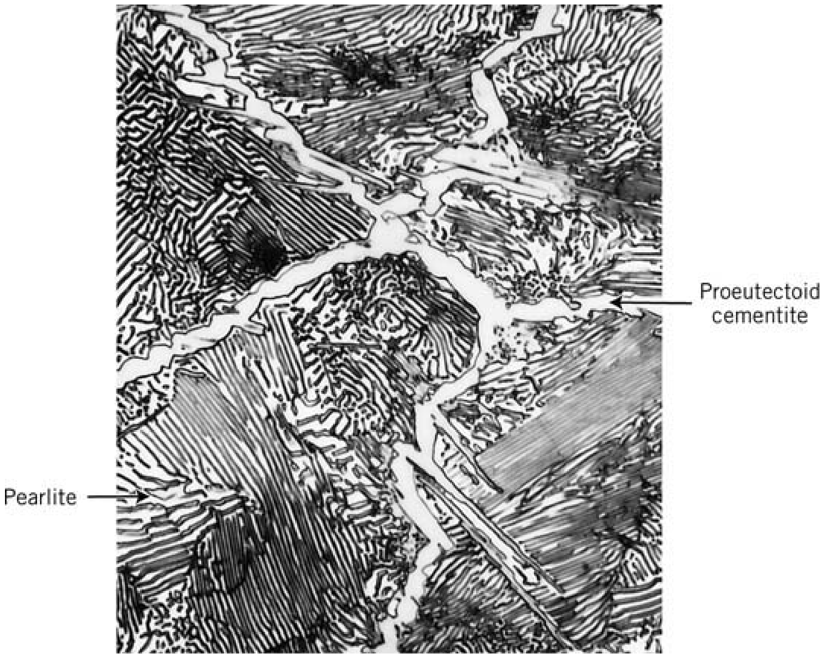
$w_{Fe_3C} = r/(r+s)$

$w_\gamma = (1 - w_{Fe_3C})$

$w_{pearlite} = w_\gamma$

$w_\alpha = S/(R+S)$

$w_{Fe_3C} = (1 - w_\alpha)$



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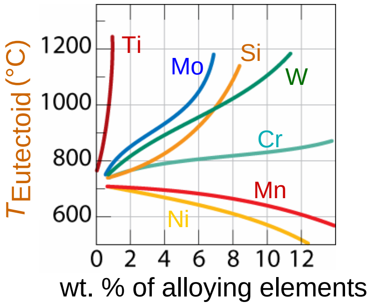
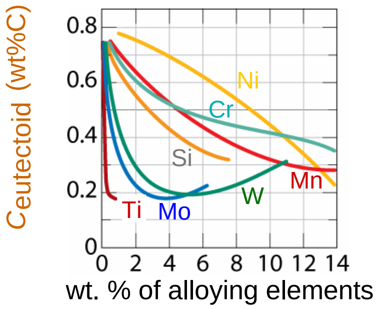
Alloying Steel with More Elements

- $T_{\text{eutectoid}}$ changes:



- $C_{\text{eutectoid}}$ changes:



Summary

- **Phase diagrams are useful tools to determine for a given *T* and composition of the system**
  - **the number and types of phases,**
  - **the wt% of each phase,**
  - **and the composition of each phase**

- **Alloying to produce a solid solution usually**
  - **increases the tensile strength (*TS*)**
  - **decreases the ductility.**

- **Binary eutectics and binary eutectoids allow for a range of microstructures.**

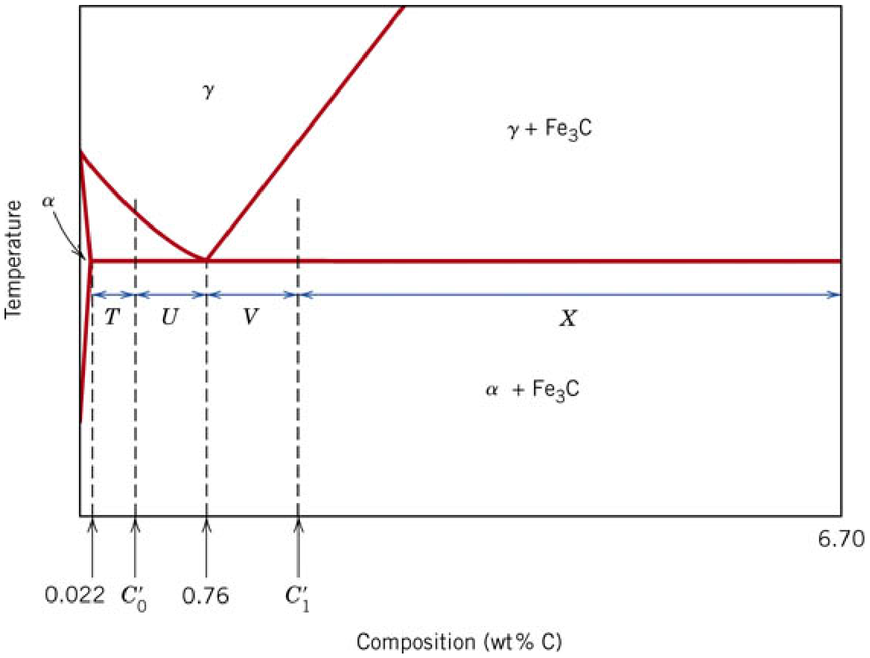
Example: Phase Equilibria

For a 99.6 wt% Fe-0.40 wt% C at a temperature just below the eutectoid, determine the following

a) composition of Fe_3C and ferrite (α)

b) the amount of carbide (cementite) in grams that forms per 100 g of steel

c) the amount of pearlite and pro-eutectoid ferrite (α)



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Phase Equilibria

Solution: a) composition of Fe_3C and ferrite (α)

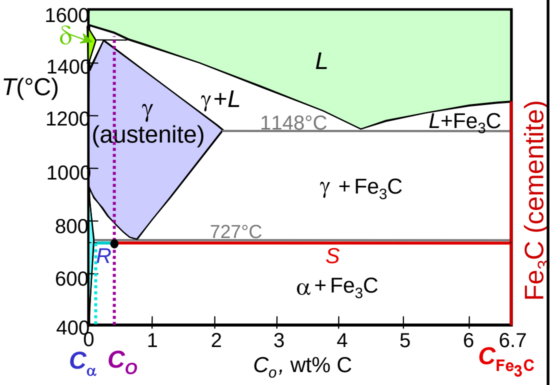
b) the amount of carbide (cementite) in grams that forms per 100 g of steel

C_O = 0.40 wt% C
C_α = 0.022 wt% C
C_{Fe_3C} = 6.70 wt% C

$$\frac{Fe_3C}{Fe_3C+\alpha} = \frac{C_o - C_\alpha}{C_{Fe_3C} - C_\alpha} x100$$

$$= \frac{0.4-0.022}{6.7-0.022} x\,100 = 5.7g$$

$$\boxed{\begin{array}{l} Fe_3C = 5.7\text{ g} \\ \alpha = 94.3\text{ g} \end{array}}$$



Phase Equilibria

c. the amount of pearlite and proeutectoid ferrite (α)

note: amount of pearlite = amount of γ just above T_E

C_o = 0.40 wt% C

C_α = 0.022 wt% C

$C_{pearlite} = C_\gamma$ = 0.76 wt% C

$$\frac{\gamma}{\gamma+\alpha} = \frac{C_o - C_\alpha}{C_\gamma - C_\alpha} \text{ x } 100 = 51.2 \text{ g}$$

pearlite = 51.2 g
proeutectoid α = 48.8 g