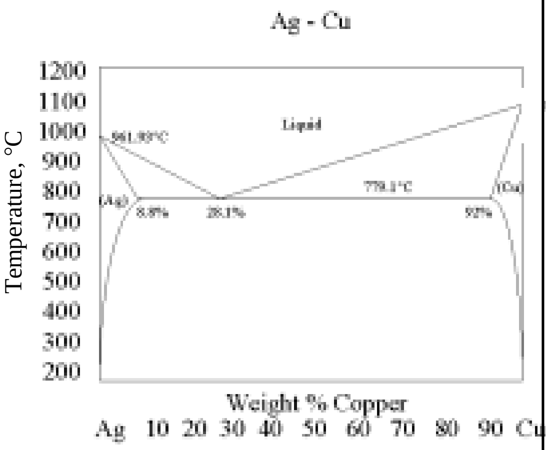
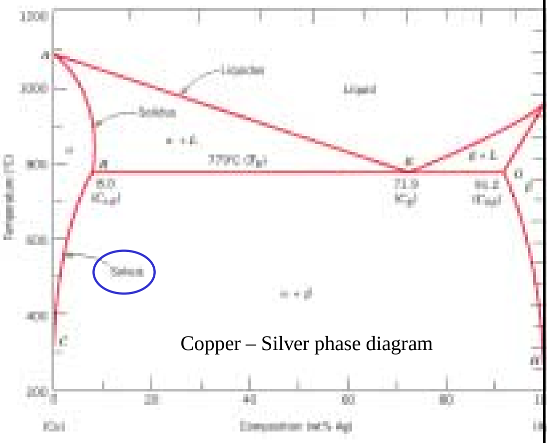
Binary Eutectic Systems (I)

alloys with limited solubility



Binary Eutectic Systems (II)



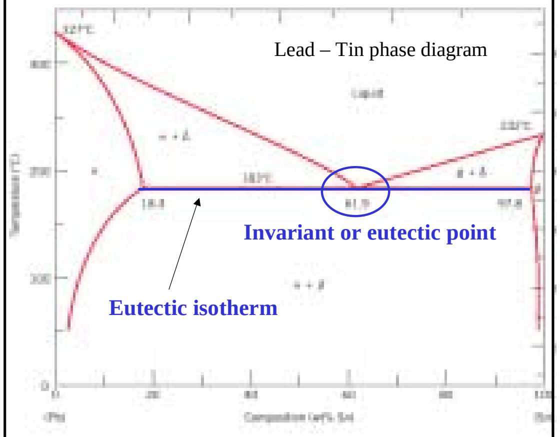
Copper – Silver phase diagram

Three single phase regions (α - solid solution of Ag in Cu matrix, β = solid solution of Cu in Ag marix, L - liquid)

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

Solvus line separates one solid solution from a mixture of solid solutions. **Solvus line shows limit of solubility**

Binary Eutectic Systems (III)



Lead – Tin phase diagram

Invariant or eutectic point

Eutectic isotherm

Eutectic or invariant point - Liquid and two solid phases co-exist in equilibrium at the eutectic composition CE and the eutectic temperature T_E.

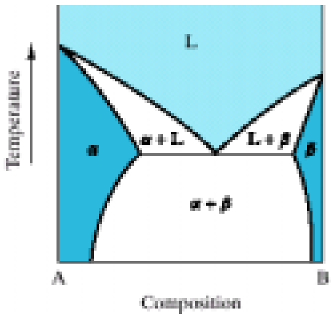
Eutectic isotherm - the horizontal solidus line at T_E.

Binary Eutectic Systems (IV)

Eutectic reaction – transition between liquid and mixture of two solid phases, α + β at eutectic concentration C_E.

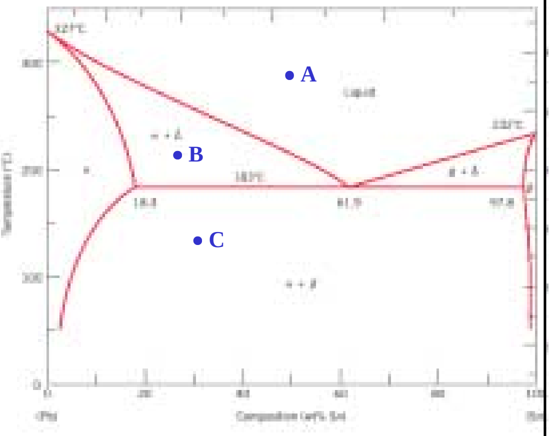
The melting point of the eutectic alloy is lower than that of the components (*eutectic* = *easy to melt in Greek*).

At most two phases can be in equilibrium within a phase field. Three phases (L, α, β) may be in equilibrium only only at a few points along the eutectic isotherm. Single-phase regions are separated by 2-phase regions.



Binary Eutectic Systems (V)

Compositions and relative amounts of phases are determined from the same tie lines and lever rule, as for isomorphous alloys

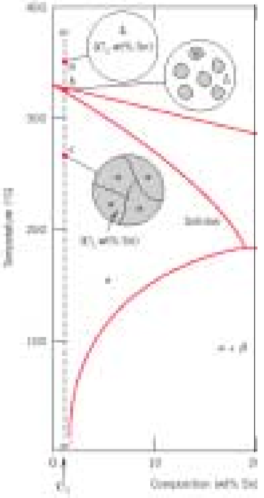


For points A, B, and C calculate the compositions (wt. %) and relative amounts (mass fractions) of phases present.

Development of microstructure in eutectic alloys (I)

Several different types of microstructure can be formed in slow cooling an different compositions.

Let’s consider cooling of liquid lead – tin system at different compositions.

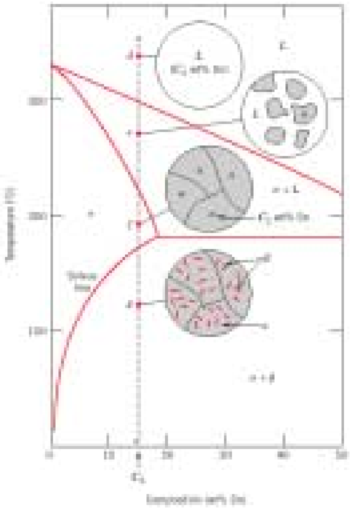


In this case of lead-rich alloy (0-2 wt. % of tin) solidification proceeds in the same manner as for isomorphous alloys (e.g. Cu-Ni) that we discussed earlier.

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

Development of microstructure in eutectic alloys (II)

At compositions between the room temperature solubility limit and the maximum solid solubility at the eutectic temperature, β phase nucleates as the α solid solubility is exceeded upon crossing the solvus line.

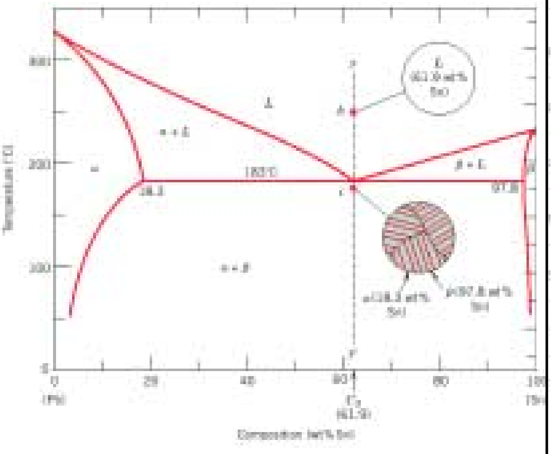


$$L$$
$$\Downarrow$$
$$\alpha + L$$
$$\Downarrow$$
$$\alpha$$
$$\Downarrow$$
$$\alpha + \beta$$

Development of microstructure in eutectic alloys (III)

Solidification at the eutectic composition (I)

No changes above the eutectic temperature T_E. At T_E the liquid transforms to α and β phases (eutectic reaction).

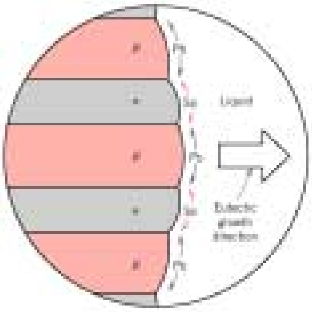


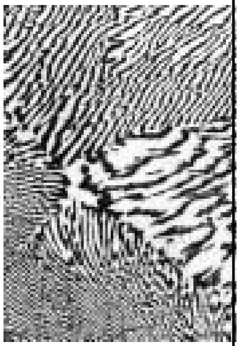
$$L \rightarrow \alpha + \beta$$

Development of microstructure in eutectic alloys (IV)

Solidification at the eutectic composition (II)

Compositions of α and β phases are very different → eutectic reaction involves redistribution of Pb and Sn atoms by atomic diffusion. This simultaneous formation of α and β phases result in a layered (lamellar) microstructure that is called **eutectic structure**.





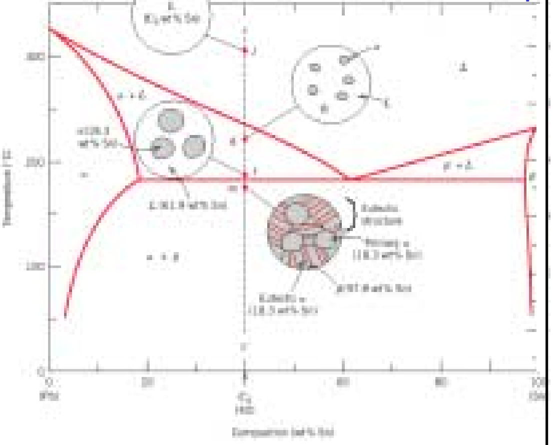
Formation of the eutectic structure in the lead-tin system. In the micrograph, the dark layers are lead-reach α phase, the light layers are the tin-reach β phase.

Development of microstructure in eutectic alloys (V)

Compositions other than eutectic but within the range of the eutectic isotherm

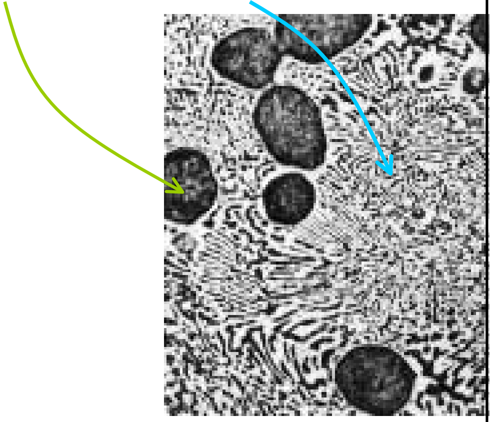
Primary α phase is formed in the α + L region, and the eutectic structure that includes layers of α and β phases (called **eutectic α** and eutectic β phases) is formed upon crossing the eutectic isotherm.

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



Development of microstructure in eutectic alloys (VI)

Microconstituent – element of the microstructure having a distinctive structure. In the case described in the previous page, microstructure consists of two microconstituents, primary α phase and the eutectic structure.



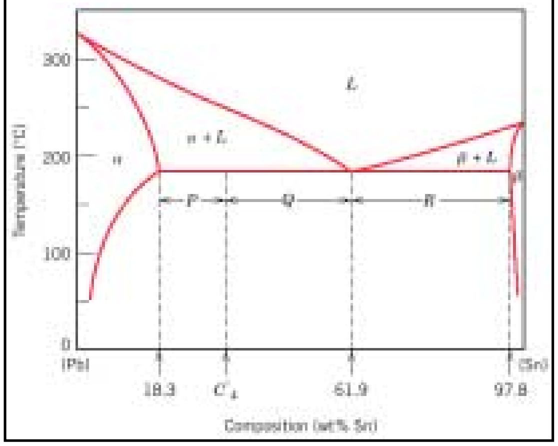
Although the eutectic structure consists of two phases, it is a microconstituent with distinct lamellar structure and fixed ratio of the two phases.

How to calculate relative amounts of microconstituents?

Eutectic microconstituent forms from liquid having eutectic composition (61.9 wt% Sn)

We can treat the eutectic as a separate phase and apply the lever rule to find the relative fractions of primary α phase (18.3 wt% Sn) and the eutectic structure (61.9 wt% Sn):

$W_e = P / (P+Q)$ (eutectic) $W_{\alpha'} = Q / (P+Q)$ (primary)

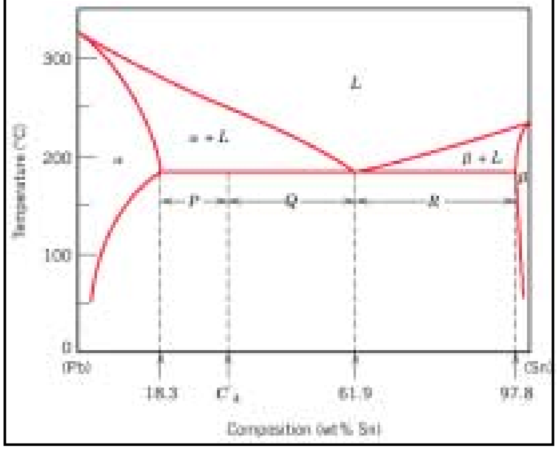


How to calculate the total amount of α phase (both eutectic and primary)?

Fraction of α phase determined by application of the lever rule across the entire α + β phase field:

W_α = (Q+R) / (P+Q+R) (α phase)

W_β = P / (P+Q+R) (β phase)

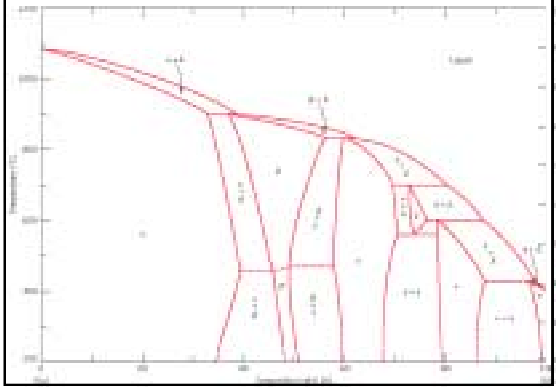


Phase Diagrams with Intermediate Phases

Eutectic systems that we have studied so far have only two solid phases (α and β) that exist near the ends of phase diagrams. These phases are called **terminal solid solutions.**

Some binary alloy systems have intermediate solid solution phases. In phase diagrams, these phases are separated from the composition extremes (0% and 100%).

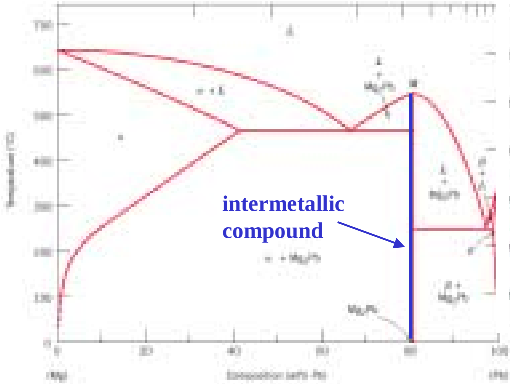
Example: in Cu-Zn, α and η are terminal solid solutions, β, β', γ, δ, ε are intermediate solid solutions.



Phase Diagrams with Intermetallic Compounds

Besides solid solutions, **intermetallic compounds**, that have precise chemical compositions can exist in some systems.

When using the lever rules, intermetallic compounds are treated like any other phase, except they appear not as a wide region but as a vertical line.



intermetallic compound

This diagram can be thought of as two joined eutectic diagrams, for Mg-Mg_2Pb and Mg_2Pb-Pb. In this case compound Mg_2Pb can be considered as a component.

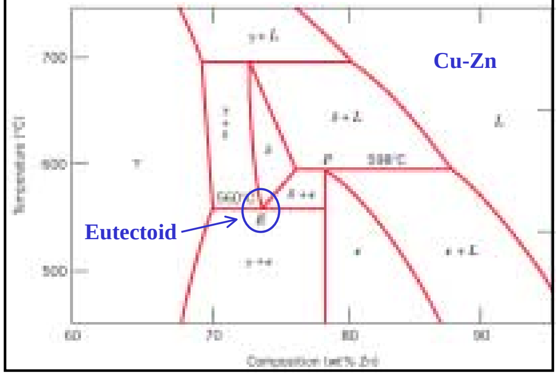
Eutectoid Reactions (I)

The **eutectoid** (*eutectic-like* in Greek) reaction is similar to the eutectic reaction but occurs from one solid phase to two new solid phases.

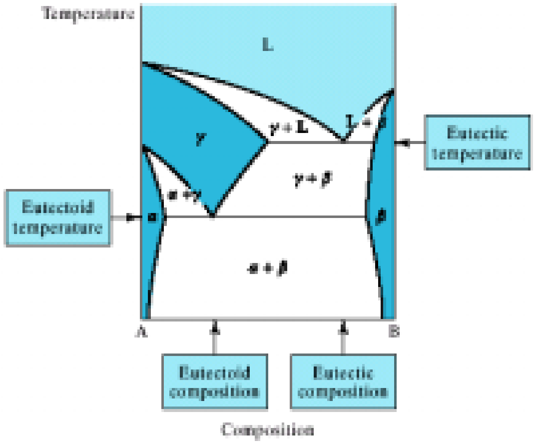
Invariant point (the eutectoid) – three **solid** phases are in equilibrium.

Upon cooling, a solid phase transforms into two other solid phases (δ ↔ γ + ε in the example below)

Looks as V on top of a horizontal tie line (eutectoid isotherm) in the phase diagram.



Eutectoid Reactions (II)



The above phase diagram contains both an eutectic reaction and its solid-state analog, an eutectoid reaction

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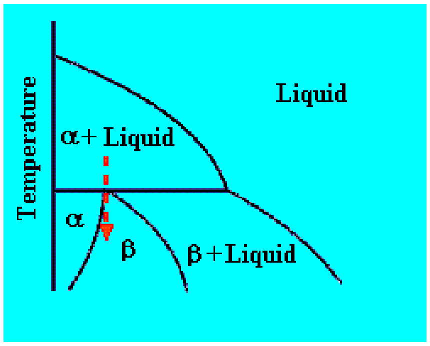
Peritectic Reactions

A **peritectic** reaction - solid phase and liquid phase will together form a second solid phase at a particular temperature and composition upon cooling - e.g. L + α ↔ β

These reactions are rather slow as the product phase will form at the boundary between the two reacting phases thus separating them, and slowing down any further reaction.

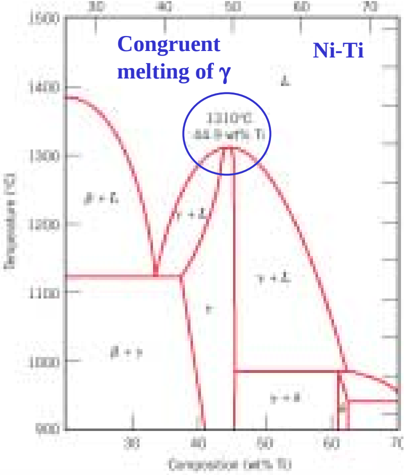


Peritectics are not as common as eutectics and eutectiods, but do occur in some alloy systems. There is one in the Fe-C system that we will consider later.

Congruent Phase Transformations

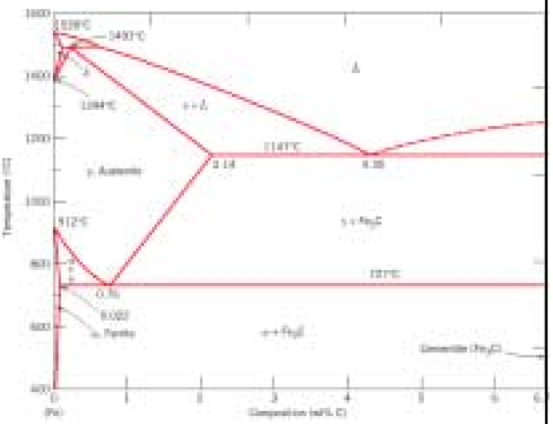
A congruent transformation involves no change in composition (e.g., allotropic transformation such as α-Fe to γ-Fe or melting transitions in pure solids).

For an incongruent transformation, at least one phase changes composition (e.g. eutectic, eutectoid, peritectic reactions).



The Iron–Iron Carbide (Fe–Fe_3C) Phase Diagram

In their simplest form, steels are alloys of Iron (Fe) and Carbon (C). The Fe-C phase diagram is a fairly complex one, but we will only consider the steel part of the diagram, up to around 7% Carbon.



Phases in Fe–Fe_3C Phase Diagram

- **α-ferrite - solid solution of C in BCC Fe**
  - Stable form of iron at room temperature.
  - The maximum solubility of C is 0.022 wt%
  - Transforms to FCC γ-austenite at 912 °C
- **γ-austenite - solid solution of C in FCC Fe**
  - The maximum solubility of C is 2.14 wt %.
  - Transforms to BCC δ-ferrite at 1395 °C
  - Is not stable below the eutectic temperature (727 ° C) unless cooled rapidly (Chapter 10)
- **δ-ferrite solid solution of C in BCC Fe**
  - The same structure as α-ferrite
  - Stable only at high T, above 1394 °C
  - Melts at 1538 °C
- **Fe_3C (iron carbide or cementite)**
  - This intermetallic compound is metastable, it remains as a compound indefinitely at room T, but decomposes (very slowly, within several years) into α-Fe and C (graphite) at 650 - 700 °C
- **Fe-C liquid solution**

A few comments on Fe–Fe_3C system

C is an interstitial impurity in Fe. It forms a solid solution with α, γ, δ phases of iron

Maximum solubility in BCC α-ferrite is limited (max. 0.022 wt% at 727 °C) - BCC has relatively small interstitial positions

Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C - FCC has larger interstitial positions

Mechanical properties: Cementite is very hard and brittle - can strengthen steels. Mechanical properties also depend on the microstructure, that is, how ferrite and cementite are mixed.

Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic

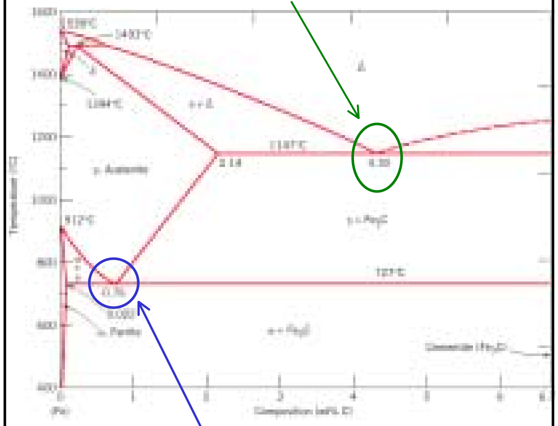
Classification. Three types of ferrous alloys:

- Iron: less than 0.008 wt % C in α–ferrite at room T
- Steels: 0.008 - 2.14 wt % C (usually < 1 wt %) α-ferrite + Fe_3C at room T (Chapter 12)
- Cast iron: 2.14 - 6.7 wt % (usually < 4.5 wt %)

Eutectic and eutectoid reactions in Fe–Fe_3C

Eutectic: 4.30 wt% C, 1147 °C

$L \leftrightarrow \gamma + Fe_3C$



Eutectoid: 0.76 wt%C, 727 °C

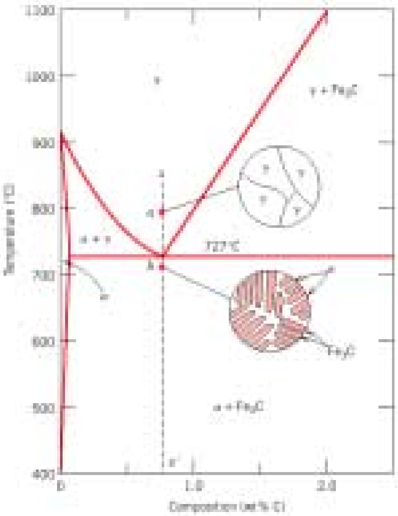
$\gamma(0.76 \text{ wt\% C}) \leftrightarrow \alpha\ (0.022 \text{ wt\% C}) + Fe_3C$

Eutectic and eutectoid reactions are very important in heat treatment of steels

Development of Microstructure in Iron - Carbon alloys

Microstructure depends on composition (carbon content) and heat treatment. In the discussion below we consider slow cooling in which equilibrium is maintained.

Microstructure of eutectoid steel (I)

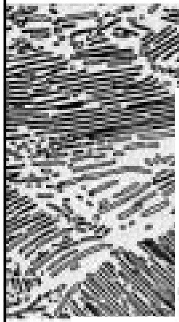


Microstructure of eutectoid steel (II)

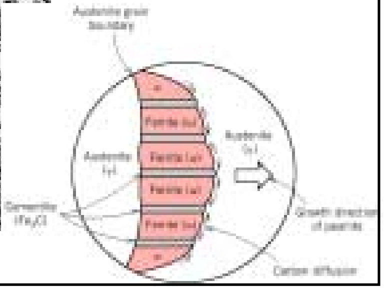
When alloy of eutectoid composition (0.76 wt % C) is cooled slowly it forms **perlite**, a lamellar or layered structure of two phases: α-ferrite and cementite (Fe_3C)

The layers of alternating phases in pearlite are formed for the same reason as layered structure of eutectic structures: redistribution C atoms between ferrite (0.022 wt%) and cementite (6.7 wt%) by atomic diffusion.

Mechanically, pearlite has properties intermediate to soft, ductile ferrite and hard, brittle cementite.



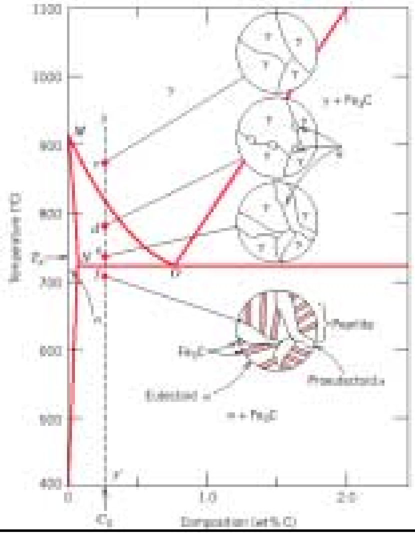
In the micrograph, the dark areas are Fe_3C layers, the light phase is α-ferrite



Microstructure of hypoeutectoid steel (I)

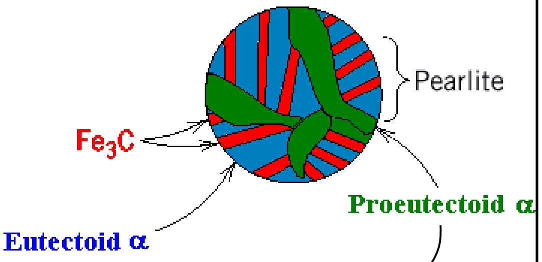
Compositions to the left of eutectoid (0.022 - 0.76 wt % C) **hypoeutectoid** (*less than eutectoid* -Greek) alloys.

$$\gamma \rightarrow \alpha + \gamma \rightarrow \alpha + Fe_3C$$



Microstructure of hypoeutectoid steel (II)

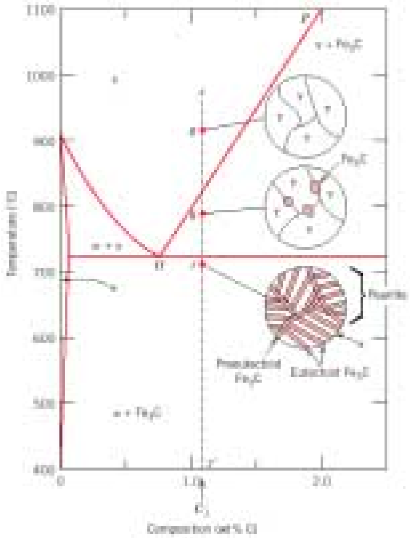
Hypoeutectoid alloys contain proeutectoid ferrite (formed above the eutectoid temperature) plus the eutectoid perlite that contain eutectoid ferrite and cementite.



Microstructure of hypereutectoid steel (I)

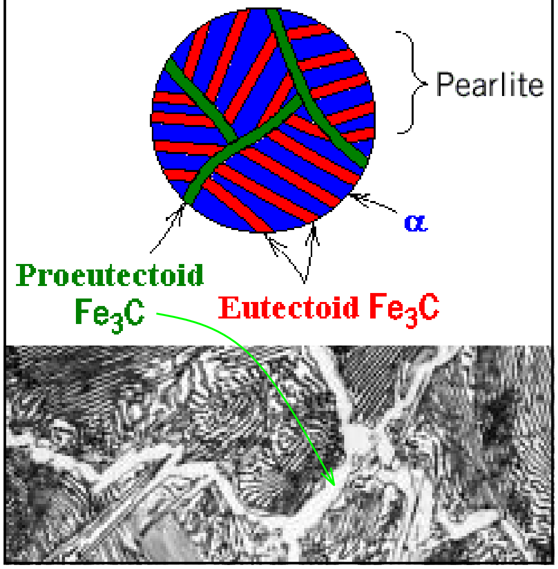
Compositions to the right of eutectoid (0.76 - 2.14 wt % C) **hypereutectoid** (*more than eutectoid* -Greek) alloys.

$$\gamma \rightarrow \gamma + Fe_3C \rightarrow \alpha + Fe_3C$$



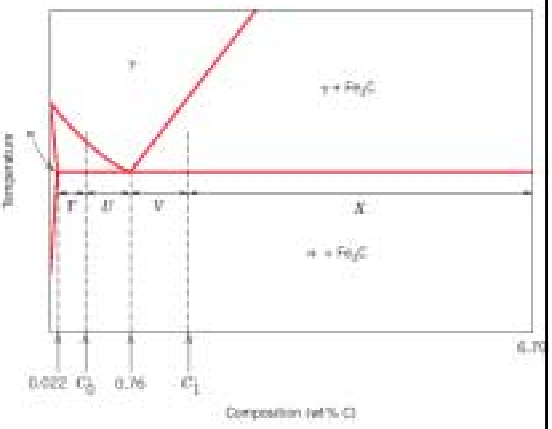
Microstructure of hypereutectoid steel (II)

Hypereutectoid alloys contain proeutectoid cementite (formed above the eutectoid temperature) plus perlite that contain eutectoid ferrite and cementite.



How to calculate the relative amounts of proeutectoid phase (α or Fe_3C) and pearlite?

Application of the lever rule with tie line that extends from the eutectoid composition (0.75 wt% C) to α – (α + Fe_3C) boundary (0.022 wt% C) for hypoeutectoid alloys and to (α + Fe_3C) – Fe_3C boundary (6.7 wt% C) for hipereutectoid alloys.



Fraction of α phase is determined by application of the lever rule across the entire (α + Fe_3C) phase field:

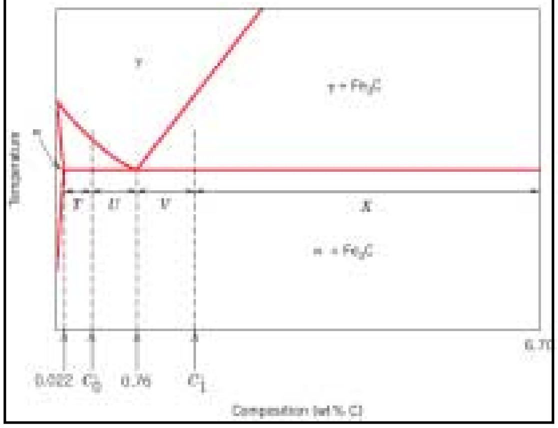
Example for hypereutectoid alloy with composition C_1

Fraction of pearlite:

$W_P = X / (V+X) = (6.7 – C_1) / (6.7 – 0.76)$

Fraction of proeutectoid cementite:

$W_{Fe3C} = V / (V+X) = (C_1 – 0.76) / (6.7 – 0.76)$



Summary

Make sure you understand language and concepts:

- Austenite
- Cementite
- Component
- Congruent transformation
- Equilibrium
- Eutectic phase
- Eutectic reaction
- Eutectic structure
- Eutectoid reaction
- Ferrite
- Hypereutectoid alloy
- Hypoeutectoid alloy
- Intermediate solid solution
- Intermetallic compound
- Invariant point
- Isomorphous
- Lever rule
- Liquidus line
- Metastable
- Microconstituent
- Pearlite
- Peritectic reaction
- Phase
- Phase diagram
- Phase equilibrium
- Primary phase
- Proeutectoid cementite
- Proeutectoid ferrite
- Solidus line
- Solubility limit
- Solvus line
- System
- Terminal solid solution
- Tie line

Reading for next class:

Chapter 10: Phase Transformations in Metals

- Kinetics of phase transformations
- Multiphase Transformations
- Phase transformations in Fe-C alloys
- Isothermal Transformation Diagrams
- Mechanical Behavior
- Tempered Martensite

Optional reading (Parts that are not covered / not tested):
10.6 Continuous Cooling Transformation Diagrams