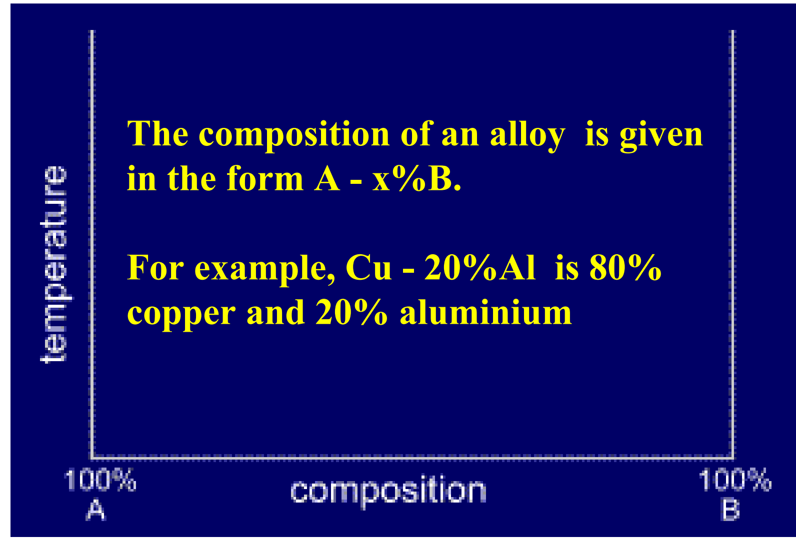
How to Build a Binary Phase Diagram: Simple Eutectic Systems

Problem:

How to represent the microstructure of an alloy given a particular temperature and composition

Solution:



A **binary phase diagram** shows the phases formed in differing mixtures of two elements over a range of temperatures.

Compositions run from 100% Element A on the left of the diagram, through all possible mixtures, to 100% Element B on the right.

Weight percentages are often used to specify the proportions of the alloying elements, but atomic percent is also used. The type of percentage is specified:

Cu - 20 wt% Al for weight percentages and
Cu - 20 at% Al for atomic percentages.

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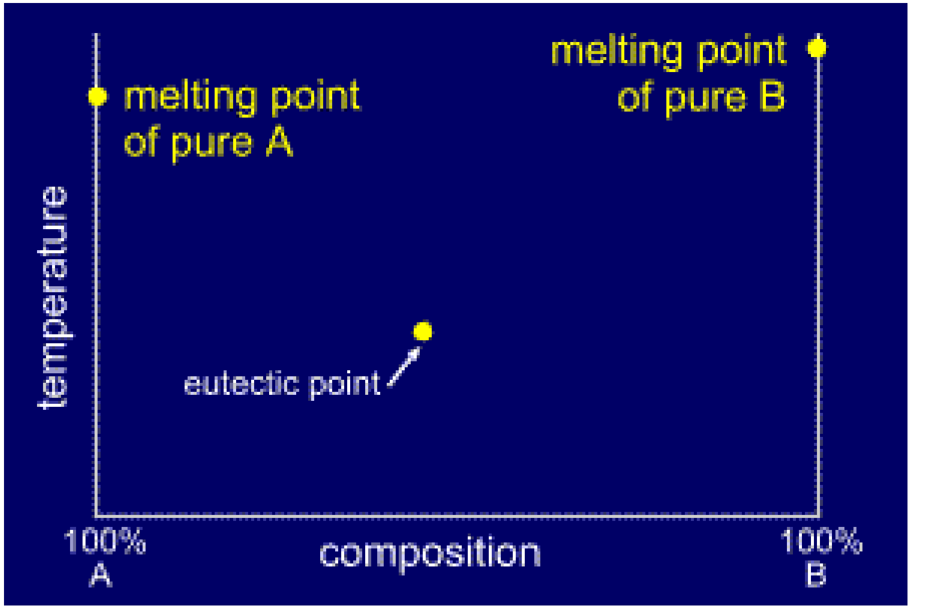
Observation:

Alloys tend to solidify over a *temperature range*, rather than at a specific temperature like pure elements.

Construction:

At each end of the phase diagram only one of the elements is present (100% A or 100% B) and therefore a specific melting point exists.



Systems:

Sometimes there is a mixture of the constituent elements which produces solidification at a single temperature like a pure element. This is called the eutectic point. The eutectic point can be found experimentally by plotting cooling rates over ranges of alloy composition.

The phase diagrams for some simple binary alloys do not have eutectic points, such as the Cu-Ni system discussed previously

How to Build a Binary Phase Diagram: Simple Eutectic Systems

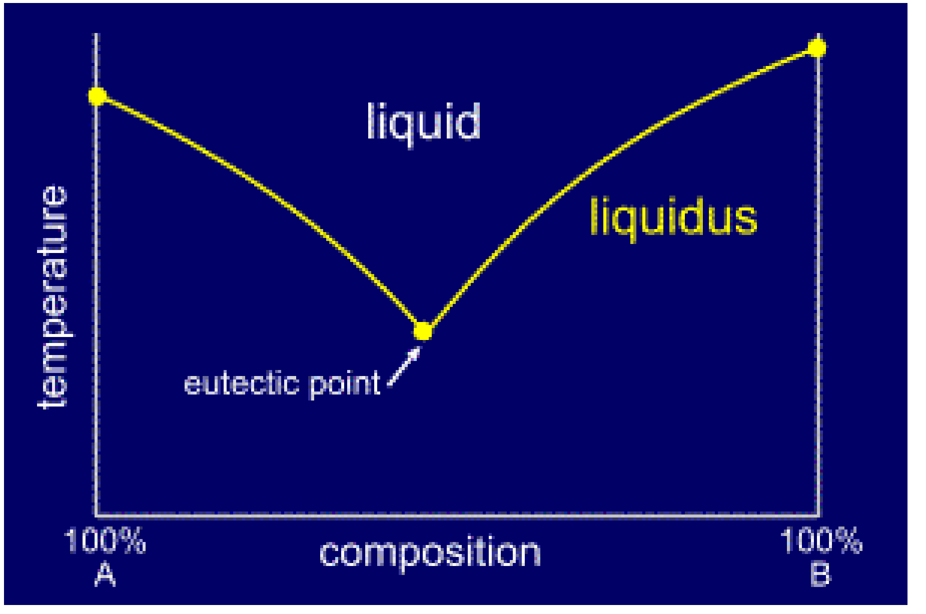
Eutectic liquidus:

By cooling alloys from the liquid state and recording their cooling rates, the temperature at which they begin to freeze can be determined and then plotted on the phase diagram.

Construction:

If a sufficient number of experiments are performed over a range of compositions, a start of solidification curve can be plotted onto the phase diagram.

This curve will join the three single solidification points and is called the liquidus line.



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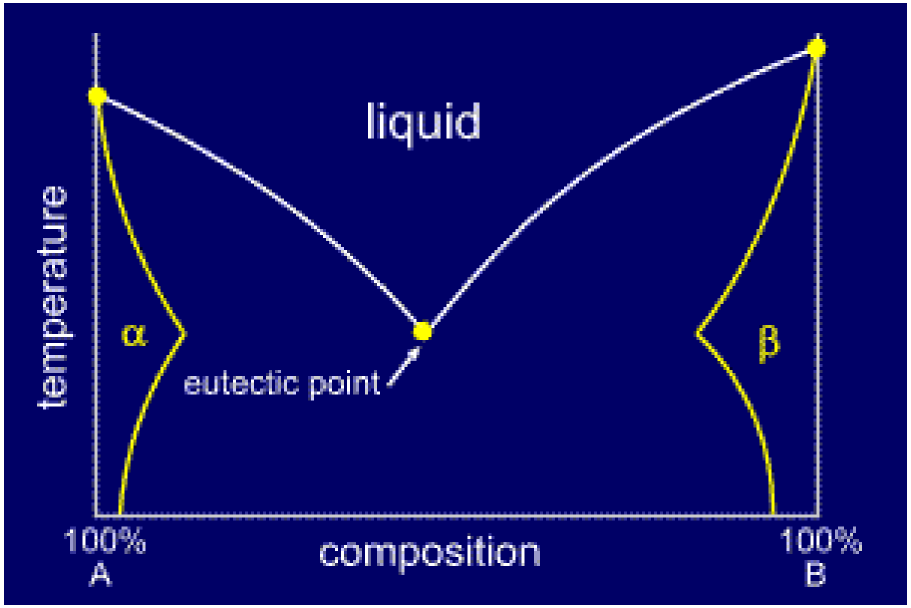
Solubility limits:

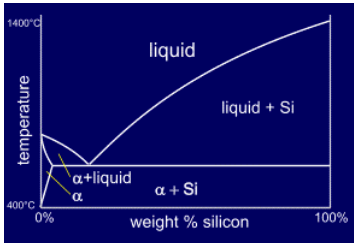
In the same way that sugar dissolves in water, it is possible for one element to dissolve in another, while both remain in a solid state. This is called **solid solubility**, and depends on crystal structure, electronegativity, valence, and atomic radius. For most solids, the solubility limit is a *few percent by weight*. This solubility limit normally depends on temperature.



Construction:

The extent of the solid solubility region is plotted on phase diagram and appropriately labeled. A solid solution of *B in A* (i.e. mostly A) is called **alpha** and a solid solution of *A in B* (i.e. mostly B) is called **beta**.

It is worthwhile to note that some pairs of elements have zero solid solubility;
a good example is Al - Si alloys, where aluminium has zero solid solubility in silicon. We say Al is insoluble in Si:



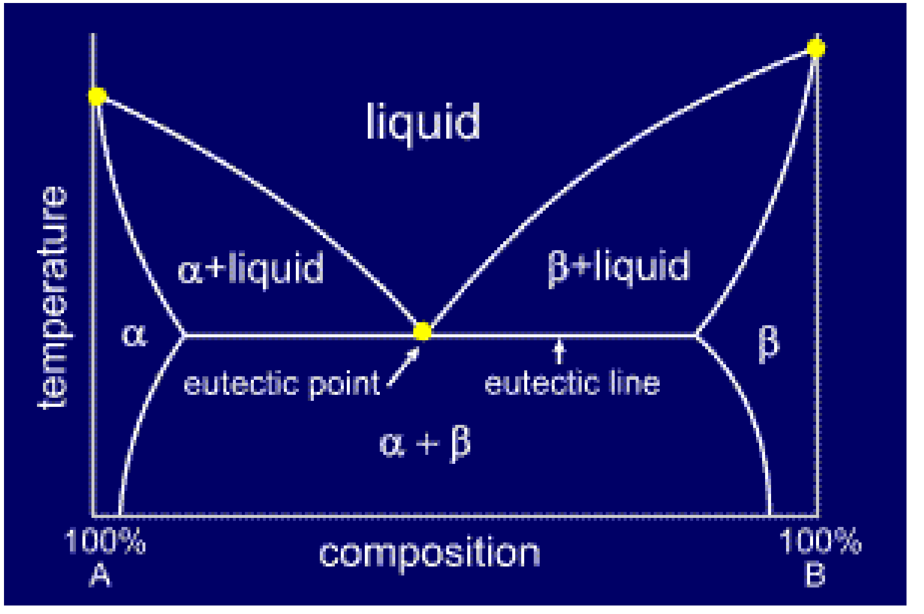
How to Build a Binary Phase Diagram: Simple Eutectic Systems

Eutectic isotherm:

If an alloy's composition does not place it within the small solid solution regions at either side of the phase diagram, the alloy will become fully solid at the eutectic temperature, shown as the eutectic isotherm on the phase diagram.

Construction:

The region below the eutectic isotherm, and outside the solid solution region, will be a solid mixture of alpha and beta, that is, a two phase region, and the diagram is labeled to reflect this.



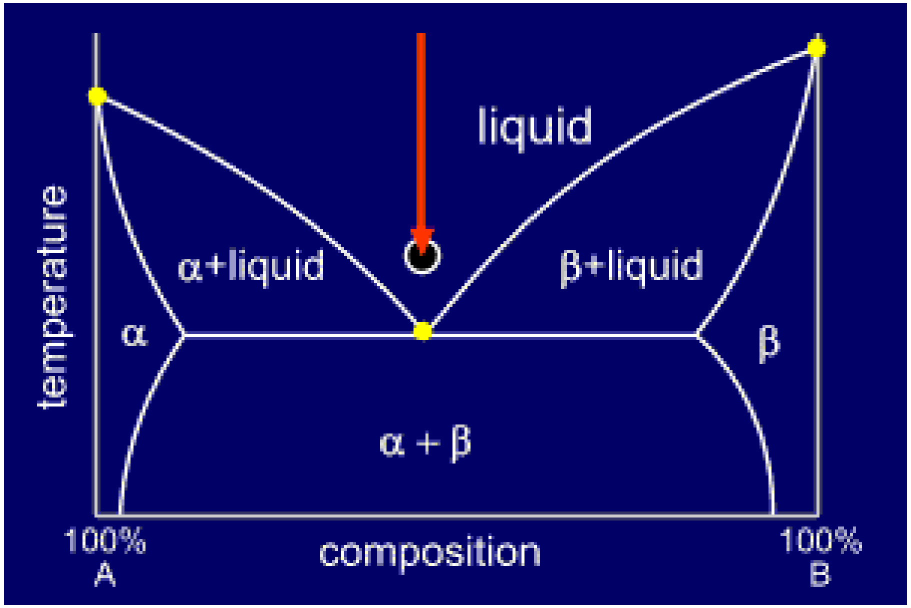
At alloy compositions and temperatures between the start of solidification and the point at which it becomes fully solid (the eutectic temperature) a *mushy* mix of either alpha or beta will co-exist as *solid lumps* within a liquid mixture of A and B. These two phase partially solid regions are marked on the phase diagram.

Binary Phase Diagrams: Simple Eutectic Systems

Eutectic solidification:

Consider a mixture of elements A and B at the eutectic composition at a high enough temperature so that the mixture is fully liquid.

Microstructure:



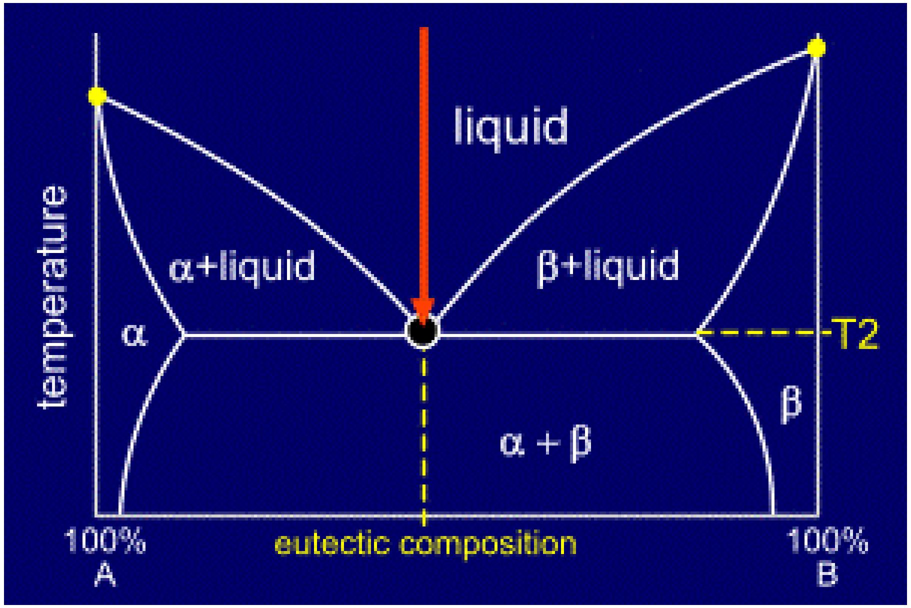
Eutectic reaction:

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

Binary Phase Diagrams: Simple Eutectic Systems

Eutectic solidification:

The mixture is *slowly cooled*, (maintaining equilibrium conditions) undergoing no phase change until it reaches temperature T2, where it starts to solidify at any nucleation site. This is termed heterogeneous nucleation.



Microstructure:

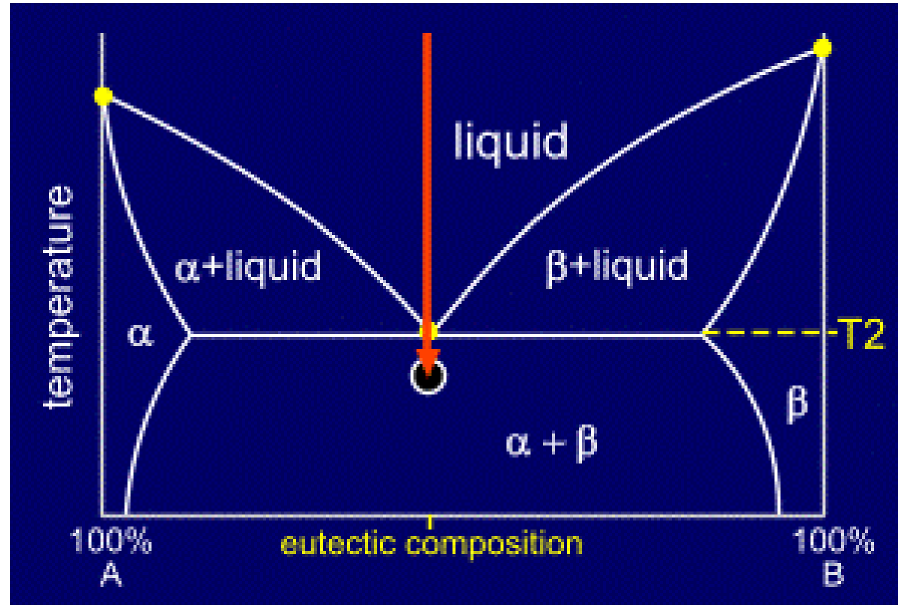
The alloy freezes into "stripes" which are alternate layers of *alpha* and *beta*. These layers are very thin, often on the order of 1 micron and the reason that the eutectic forms in this way can be understood by considering diffusion times required to form the solid. This microstructure is known as lamellar.

Binary Phase Diagrams: Simple Eutectic Systems

Eutectic solidification:

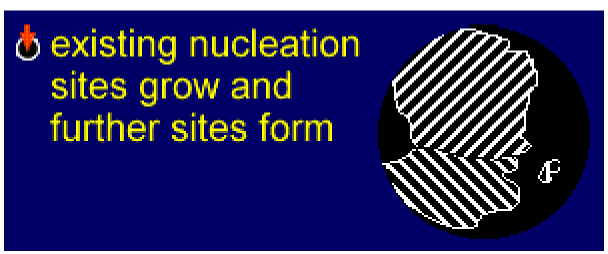
As the alloy cools below the eutectic temperature, T2, the existing nucleation sites will grow, adding *alpha to alpha* and *beta to beta*.

These nucleating and growing regions of solid alloy will form grains. Grain boundaries are formed where growing grains, which will be of differing orientations meet.



The eutectic composition solidifies, like a pure element, at a single temperature, not over a temperature range.

Microstructure:



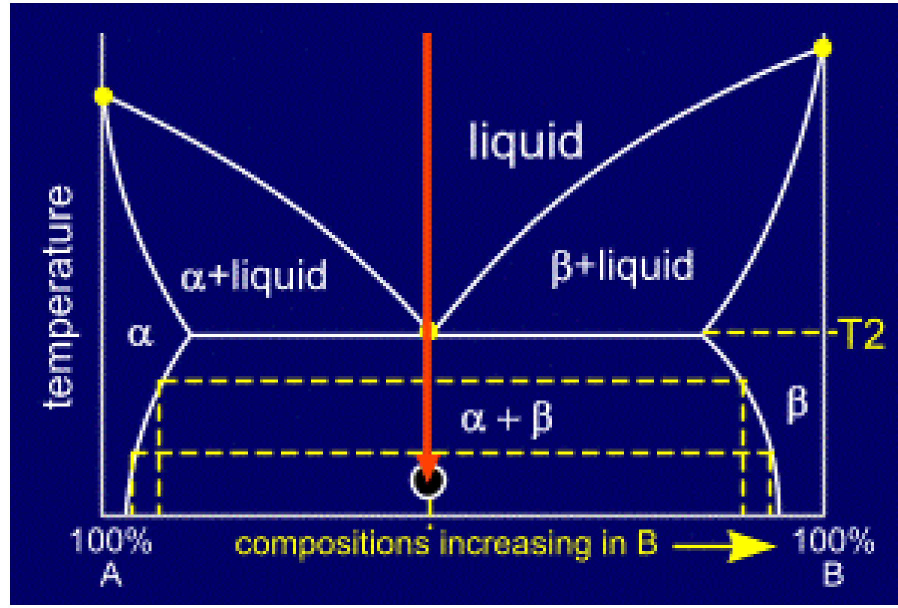
Binary Phase Diagrams: Simple Eutectic Systems

Eutectic solidification:

The entire mixture rapidly solidifies into a eutectic solid.

Looking at the phase diagram, it can be seen that the compositions of alpha and beta change with temperature.

By considering tie lines and the phase diagram, it can be seen that beta has a decreasing proportion of A in it as the temperature decreases. Similarly the proportion of B in alpha decreases.



Even though the alloy is now solid, the composition of the alpha and beta lamella must continue to change as it cools (to room temperature for example).

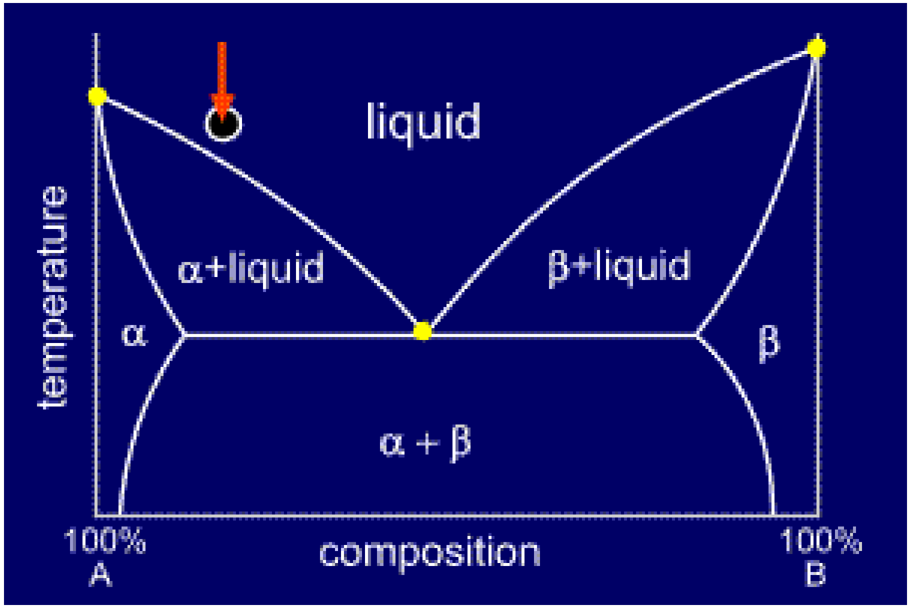
Atoms of A and B will diffuse across these lamellae to produce the equilibrium compositions of alpha and beta at a given temperature.

Microstructure:

Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

Consider a mixture of A and B so that the <u>overall composition</u> of the alloy places it to the *left* of the eutectic point. Initially the alloy is at a high enough temperature to ensure that the mixture is fully liquid.



Microstructure:

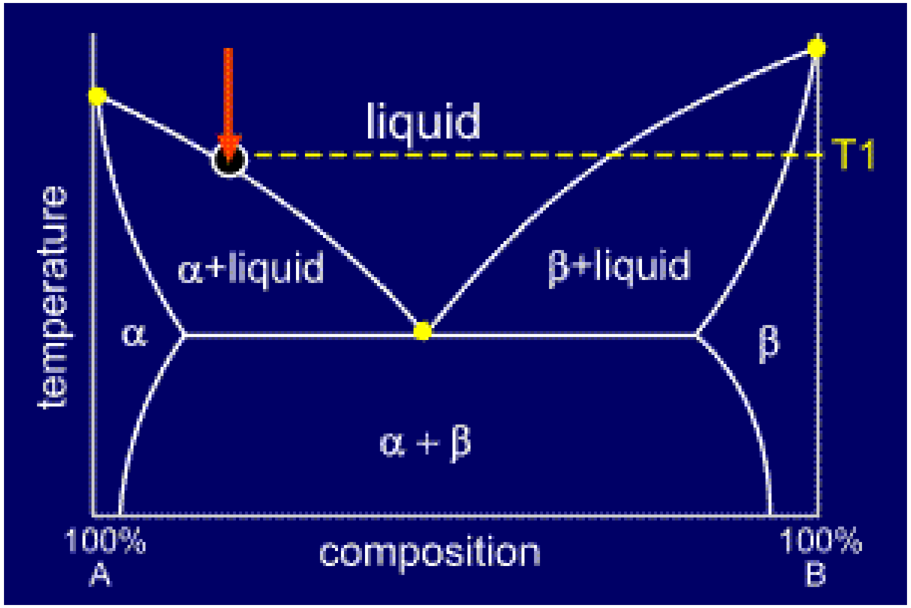
When the composition of an alloy places it at a lower composition than that of the eutectic point it is called hypo-eutectic.

If the phase diagram had been drawn the other way around, with 100%A on the right and 100%B on the left, then the same alloy would be called hyper-eutectic, since it would have a composition greater than that of the eutectic.

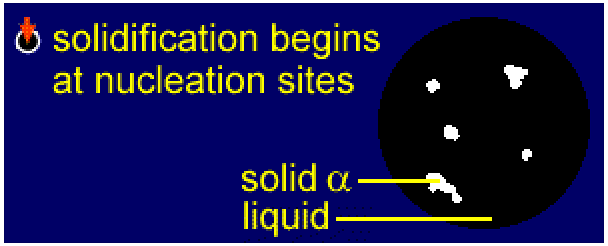
Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

The hypo-eutectic mixture is slowly cooled, undergoing no change in state until it reaches temperature T1, when it reaches the liquidus. Here, alpha phase starts to solidify at any nucleation site, such as a defect on the container wall or on an impurity particle.



Microstructure:



The alpha solidifies as dendrites, which grow to become grains of alpha.

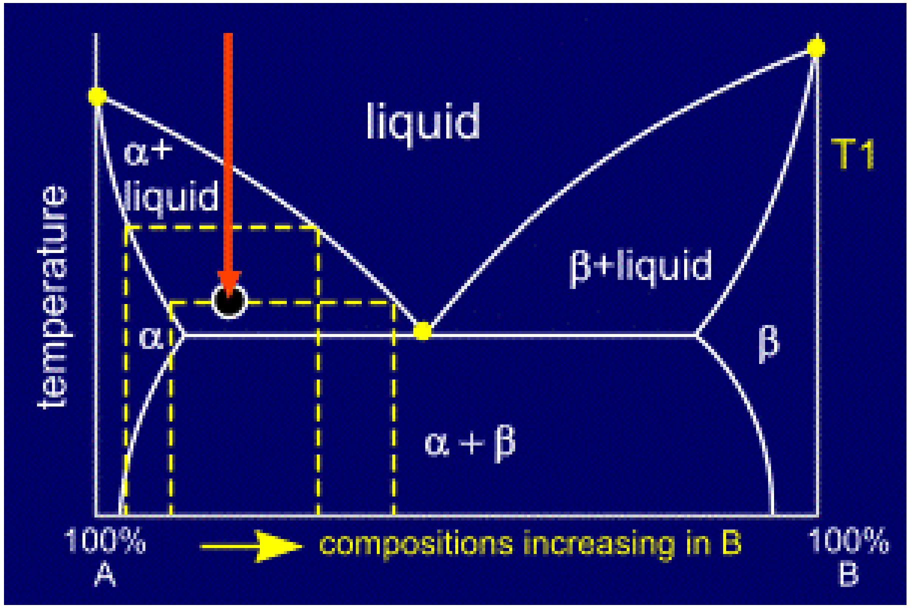
The first solid to form is called the primary solid, and in this example, would be called primary alpha.

Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

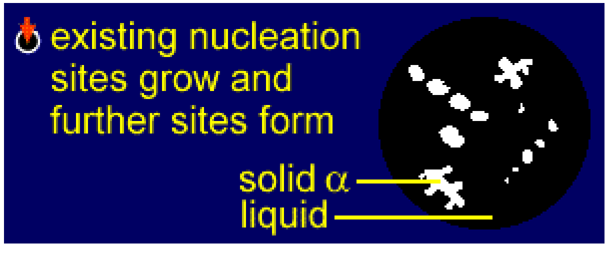
As the alloy continues to cool the existing nuclei grow (coarsen) and additional sites will continue to form within the liquid parts of the mixture.

These nucleating and growing regions of solid alloy form grains, and when these meet grain boundaries are formed. The primary alpha dendrites grow, which accounts for the shapes the alpha forms in cross sectional samples.



As the remaining liquid cools its composition becomes richer in B (following the liquidus). The composition of solid alpha also becomes richer in B, as indicated by the phase diagram. If cooling is not sufficiently slow (i.e. non-equilibrium) then B atoms will not be able to diffuse into the grains of alpha. If this is the case then microstructural "coring" will occur.

Microstructure:

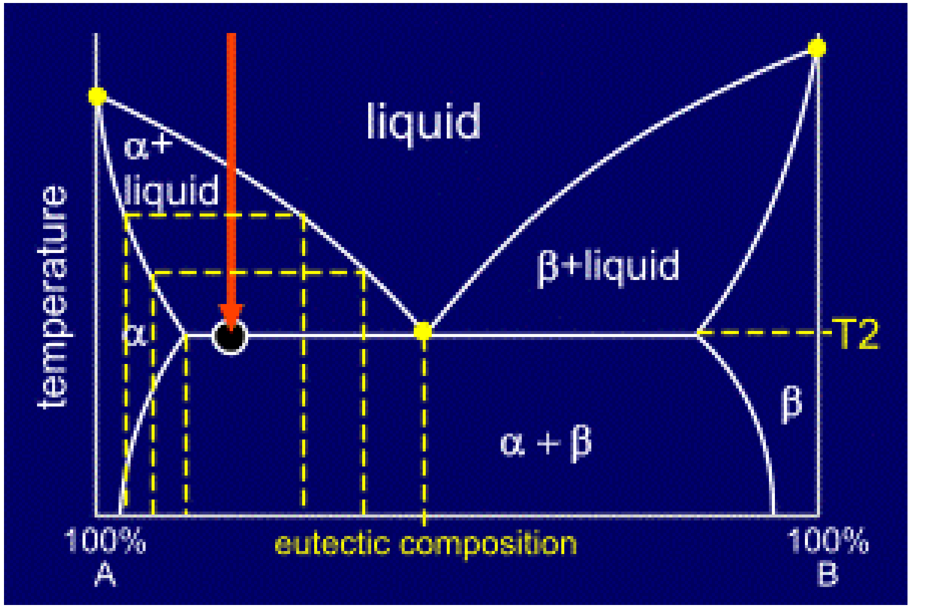


Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

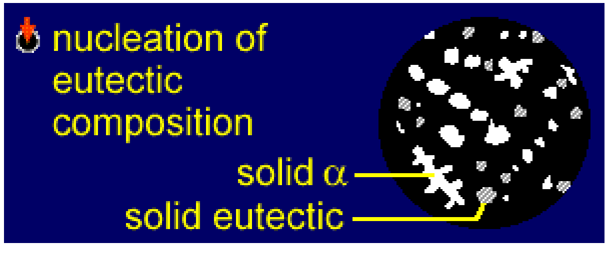
As alpha solidifies it removes A and B atoms from the remaining liquid. Alpha is mostly A (with a small amount of B) and so the remaining liquid becomes enriched in B. This continues until enough A has been removed so that the remaining liquid, following the liquidus, is of eutectic composition.

This composition will be achieved at temperature T2, at the point where the temperature crosses the eutectic line.



At this point alpha stops forming as a discrete solid and the remaining liquid solidifies into the lamellar eutectic composition of alpha and beta. Therefore, solid eutectic forms.

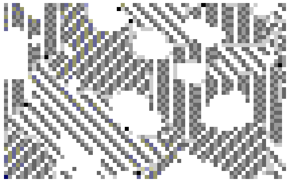
Microstructure:

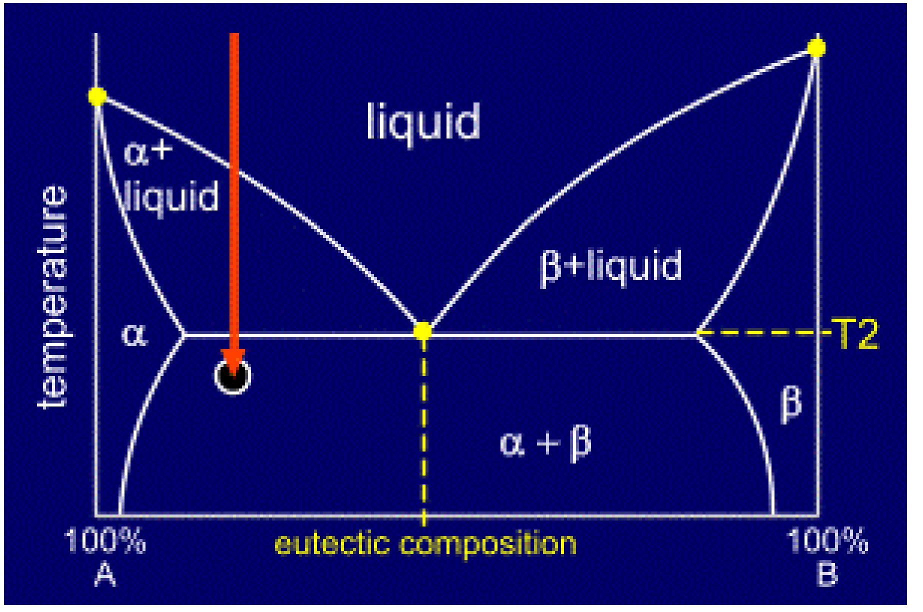


Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

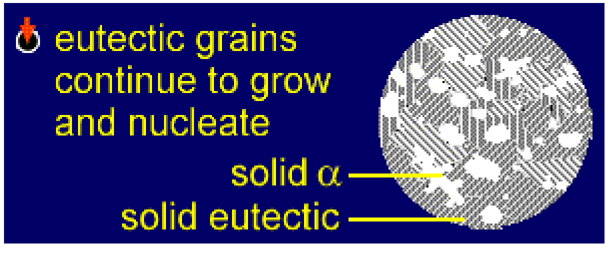
The existing eutectic nucleation sites will grow, adding alpha to the lamellae of alpha, and beta to the lamellae of beta in the eutectic regions. New sites will continue to form.





Note that, unlike the alpha solidification, it is not necessary to continue decreasing the temperature to achieve full solidification. The eutectic liquid solidifies in the same way as a pure solid, at a specific temperature.

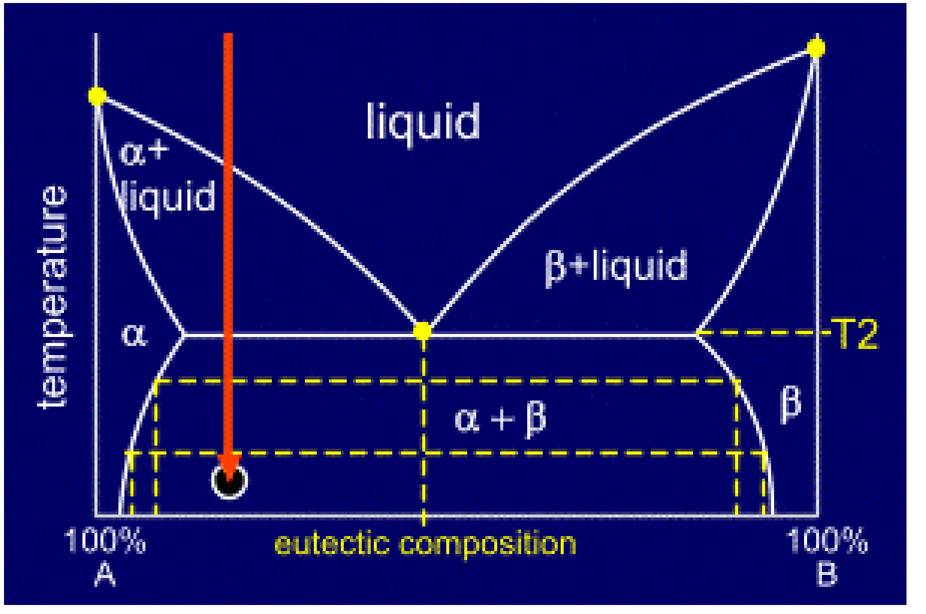
Microstructure:



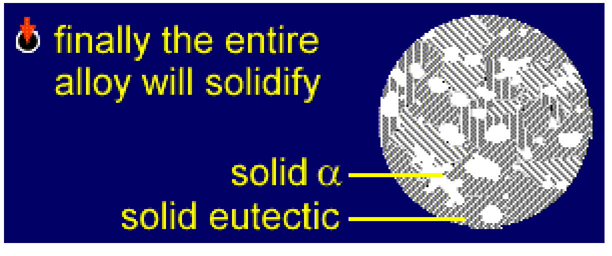
Simple Eutectic Systems: Hypo-eutectic compositions

Solidification:

The entire alloy has now solidified into a mixture comprising grains of alpha and grains of eutectic (alpha and beta in a lamellar arrangement).



Microstructure:

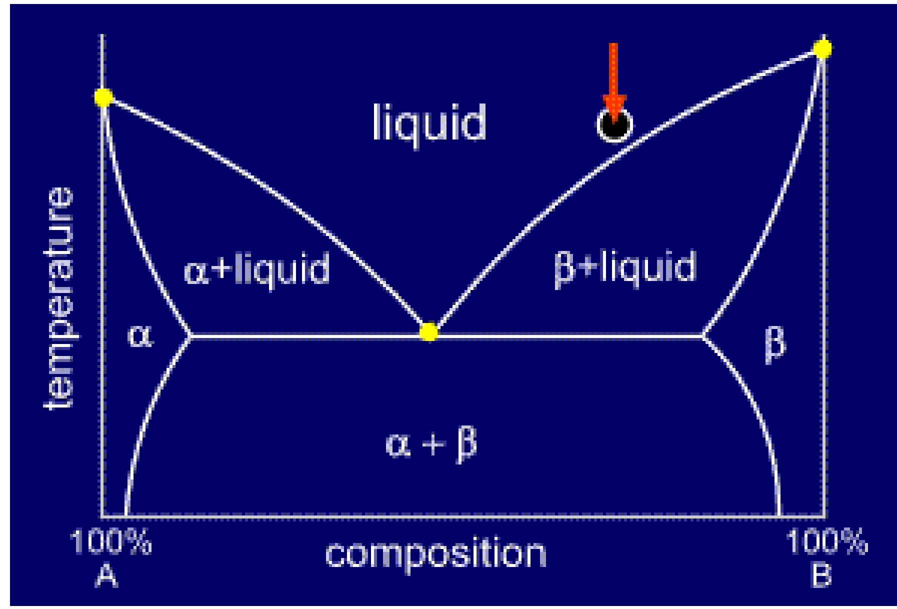


The diffusion processes through the solid, which occur as the alloy cools, are more complex than those of the eutectic case. As with a eutectic alloy, the amount of B in the alpha phase changes with temperature, and so B will have to diffuse through the alpha. This diffusion must also occur in the grains of pure alpha, as the composition of alpha also changes. This can be seen by examining the diagram.

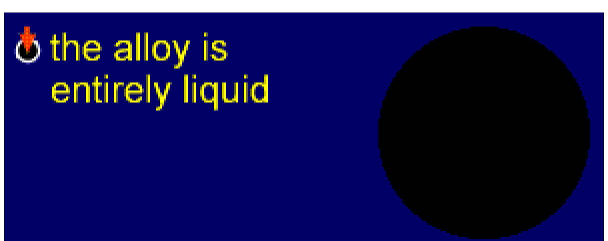
Eutectic Systems: Hyper-eutectic compositions

Solidification:

Now consider a mixture of A and B such that the overall composition of the alloy places it to the *right* of the eutectic. Initially the alloy is at a high enough temperature to ensure that the mixture is fully liquid.



Microstructure:

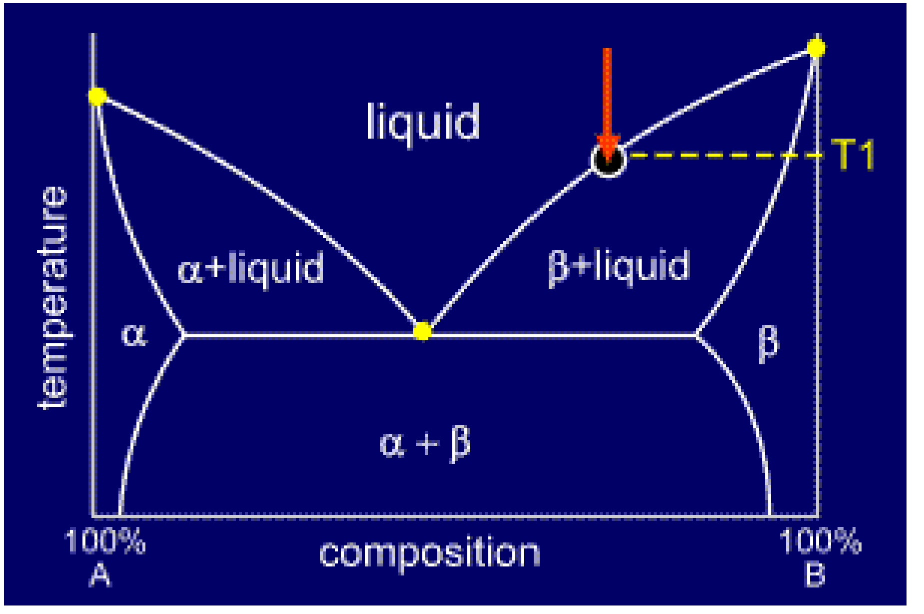


Then the composition of an alloy places it to the right of the eutectic point it is called hyper-eutectic. If the phase diagram had been drawn the other way around, with 100%A on the right and 100%B on the left, then the same alloy would be called hypo-eutectic, since it would fall to the left of the eutectic point.

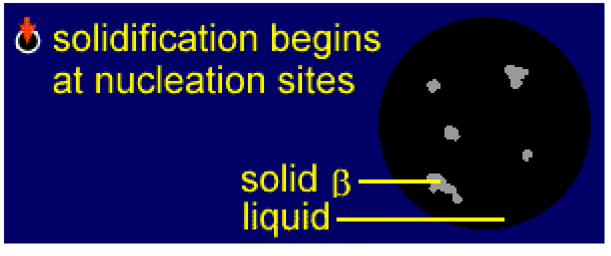
Eutectic Systems: Hyper-eutectic compositions

Solidification:

The mixture is slowly cooled, undergoing no phase change until it reaches temperature T1, when it reaches the liquidus. Here primary beta starts to nucleate at any nucleation site.



Microstructure:



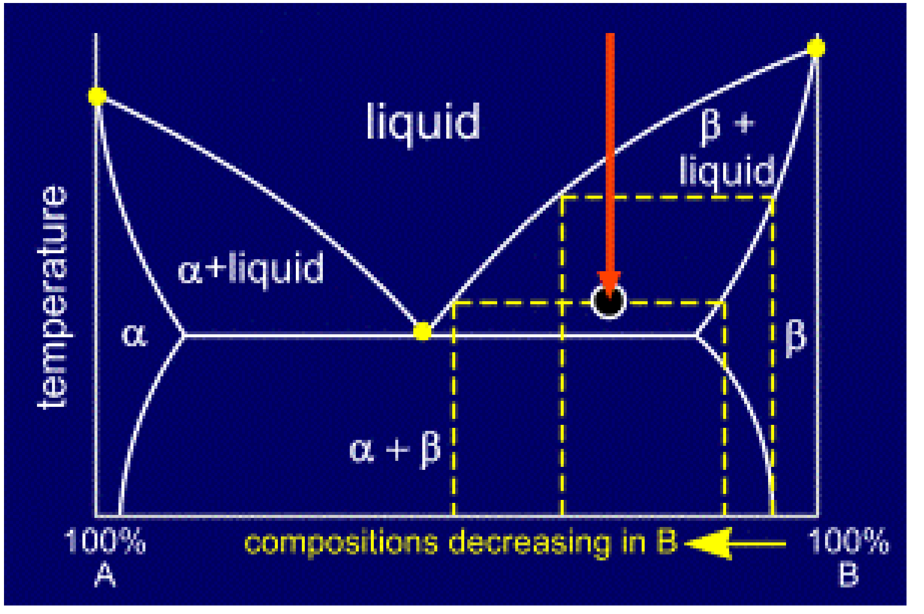
The beta solidifies as dendrites, which coarsen, or grow, to become grains of beta phase. The first solid to form is called the primary solid and so, in this case, primary beta is formed.

Eutectic Systems: Hyper-eutectic compositions

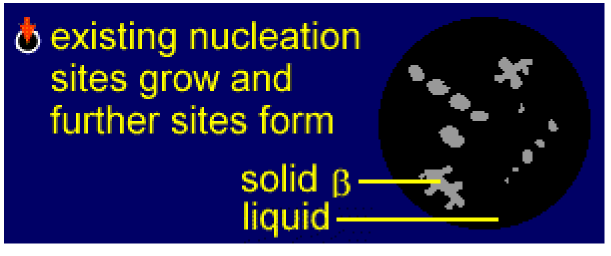
Solidification:

As the alloy cools, the existing nucleation sites will grow and further nucleation sites will form within the liquid.

These nucleating and growing regions of solid beta alloy form grains, and when these meet, grain boundaries are formed. The primary beta dendrites grow, which accounts for the shape of beta in cross sectional samples.



Microstructure:



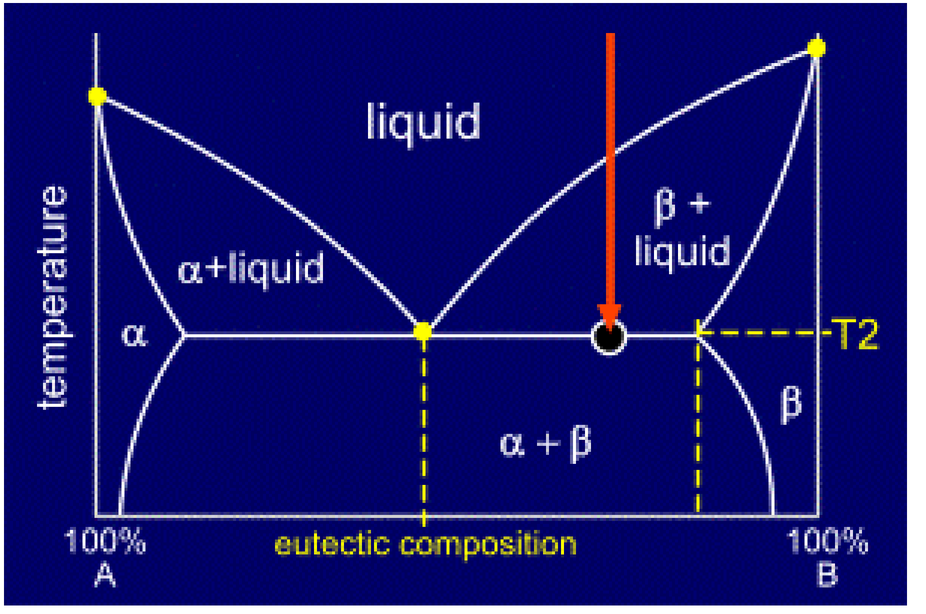
As the remaining liquid cools, its composition becomes enriched A (effectively following the liquidus). The composition of the solid beta also becomes richer in A, as shown by the phase diagram. If cooling is relatively fast (i.e. non-equilibrium) then A atoms will not be able to diffuse into the centres of the grains of beta. If this is the case then microstructural "coring" will occur.

Eutectic Systems: Hyper-eutectic compositions

Solidification:

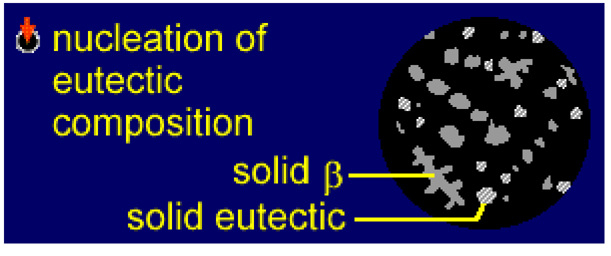
As beta solidifies, A and B atoms are removed from the remaining liquid. Beta is mostly B (with a small amount of A) and so the remaining liquid becomes enriched in A. This continues until enough B has been removed so that the remaining liquid - following the liquidus - is of eutectic composition.

This composition will be achieved at temperature T2, at the point where the temperature crosses the eutectic line.



At this point beta stops forming as a discrete solid and the remaining liquid starts to solidify into the lamellar eutectic composition of alpha and beta. Therefore, solid eutectic forms.

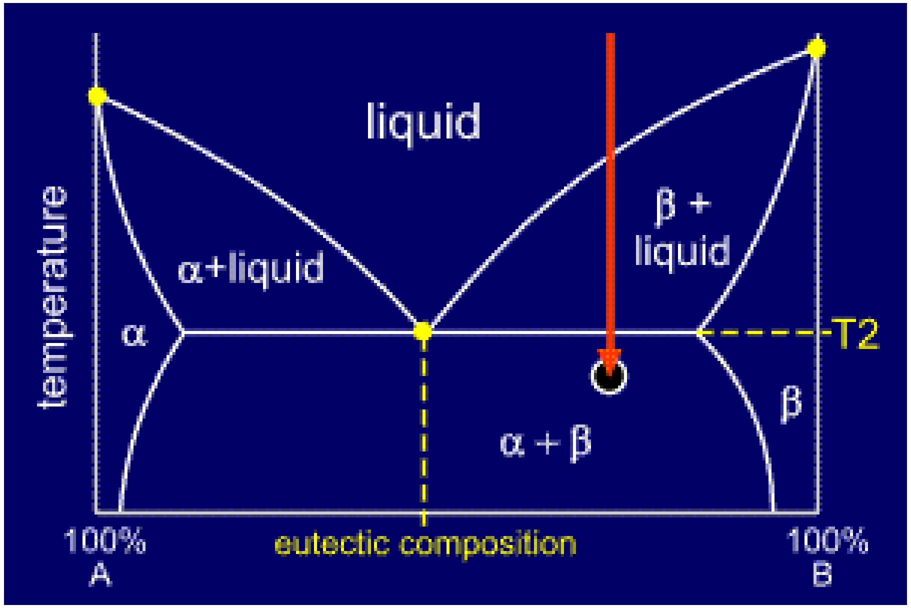
Microstructure:



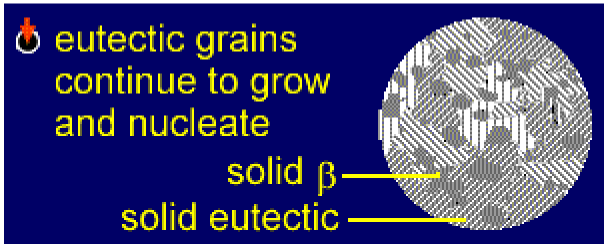
Eutectic Systems: Hyper-eutectic compositions

Solidification:

The existing eutectic nucleation sites will grow, adding alpha to the lamellae of alpha, and beta to the lamellae of beta in the eutectic regions. New sites will continue to form.



Microstructure:

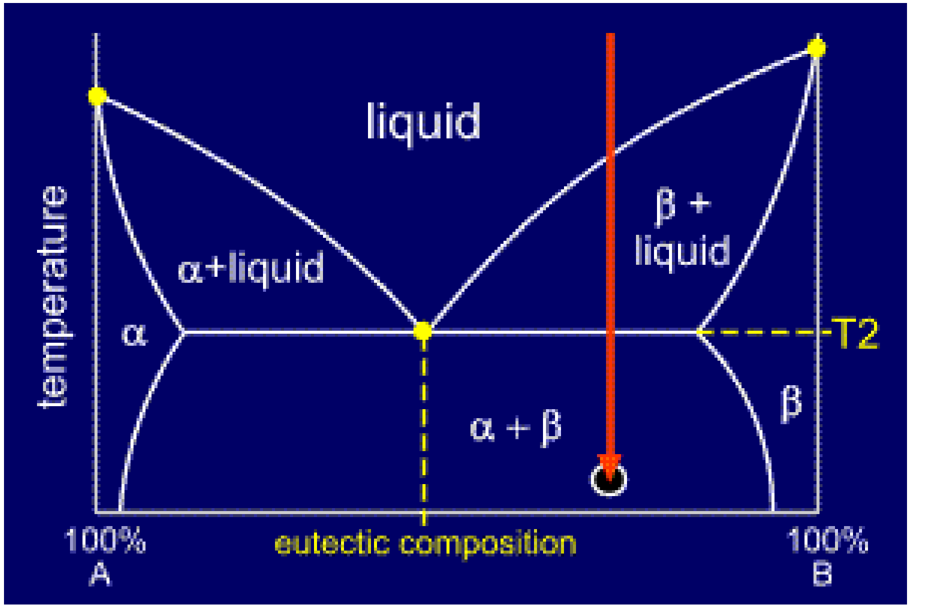


Note that, unlike the beta solidification process, it is not necessary to decrease the temperature to achieve full solidification. The eutectic solidifies in the same way as a pure solid, at a specific temperature.

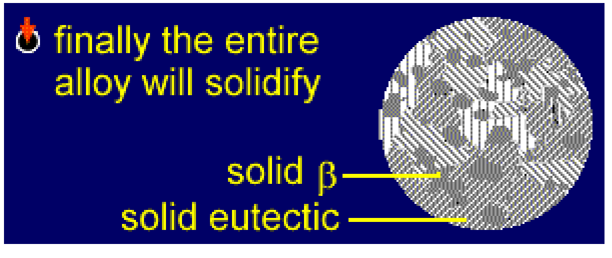
Eutectic Systems: Hyper-eutectic compositions

Solidification:

The entire alloy has now solidified into a mixture consisting of grains of beta and grains of eutectic mixture (alpha and beta). Thus, the microstructure of the solidified alloy contains two phases; one phase is beta (primary beta), the other phase is the eutectic (consisting of alternating layers of alpha and beta).



Microstructure:

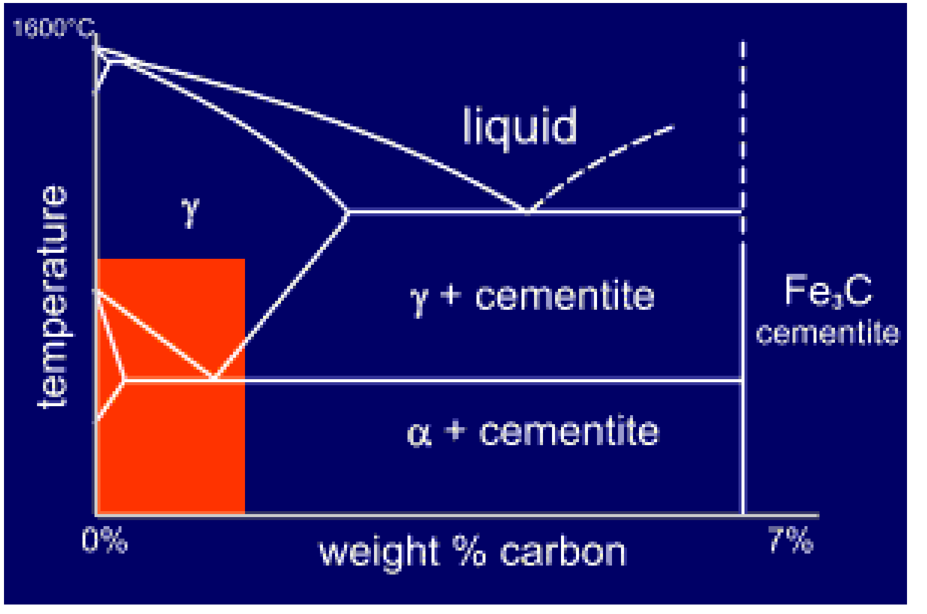


The diffusion processes through the solid, which occur as the alloy cools, are more complex than those of the eutectic case. As with a eutectic alloy, the amount of A in the beta phase changes with temperature, and so A will have to diffuse through the beta. This diffusion must also occur in the grains of pure beta, as the composition of beta also changes. This can be seen by examining the diagram.

The Fe-C system

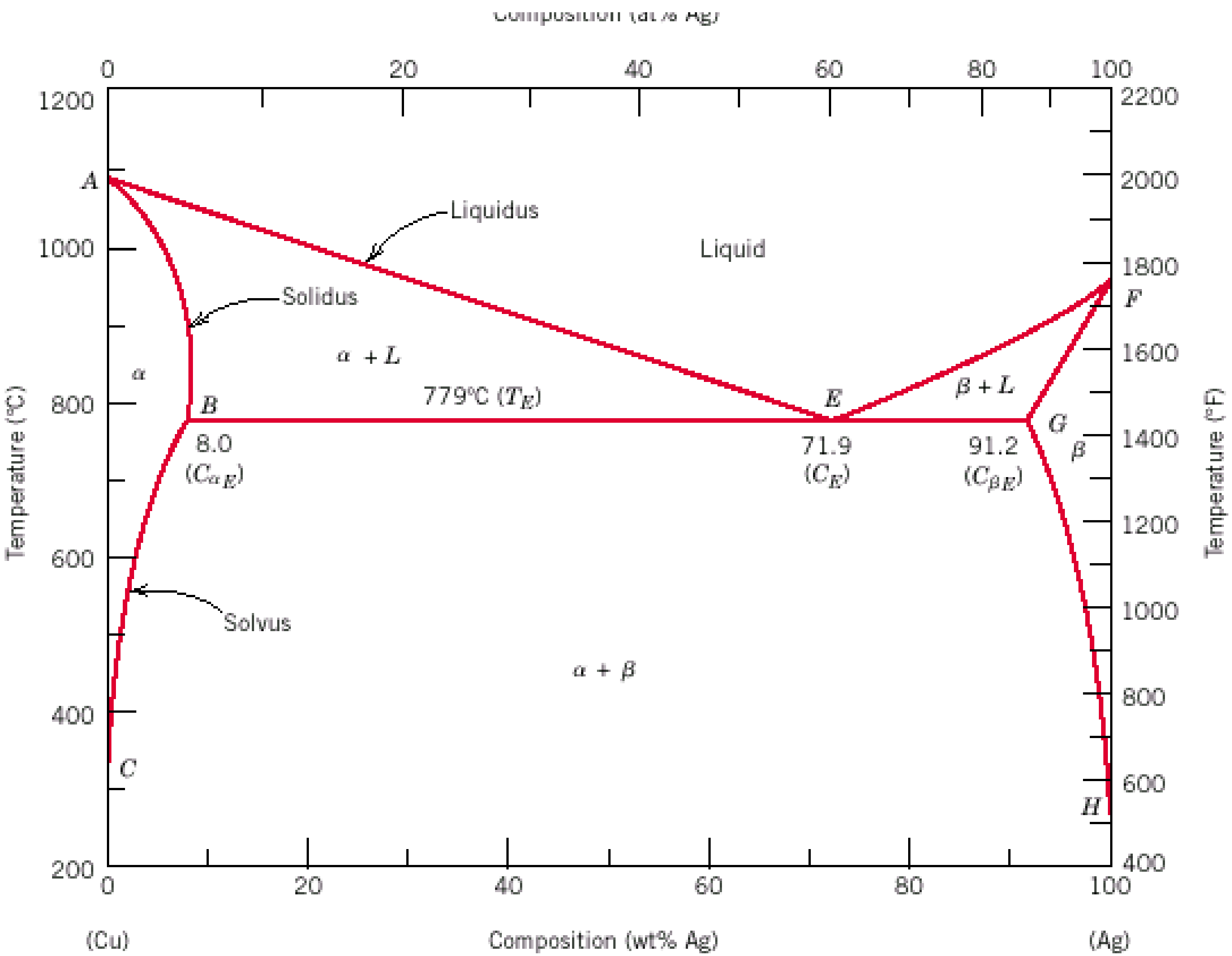
Background:

In their simplest form, steels are simply alloys of Iron (Fe) and Carbon (C). (C is an interstitial substitutional solute in Fe) The Fe-C phase diagram is shown on the right, up to around *7% Carbon*.

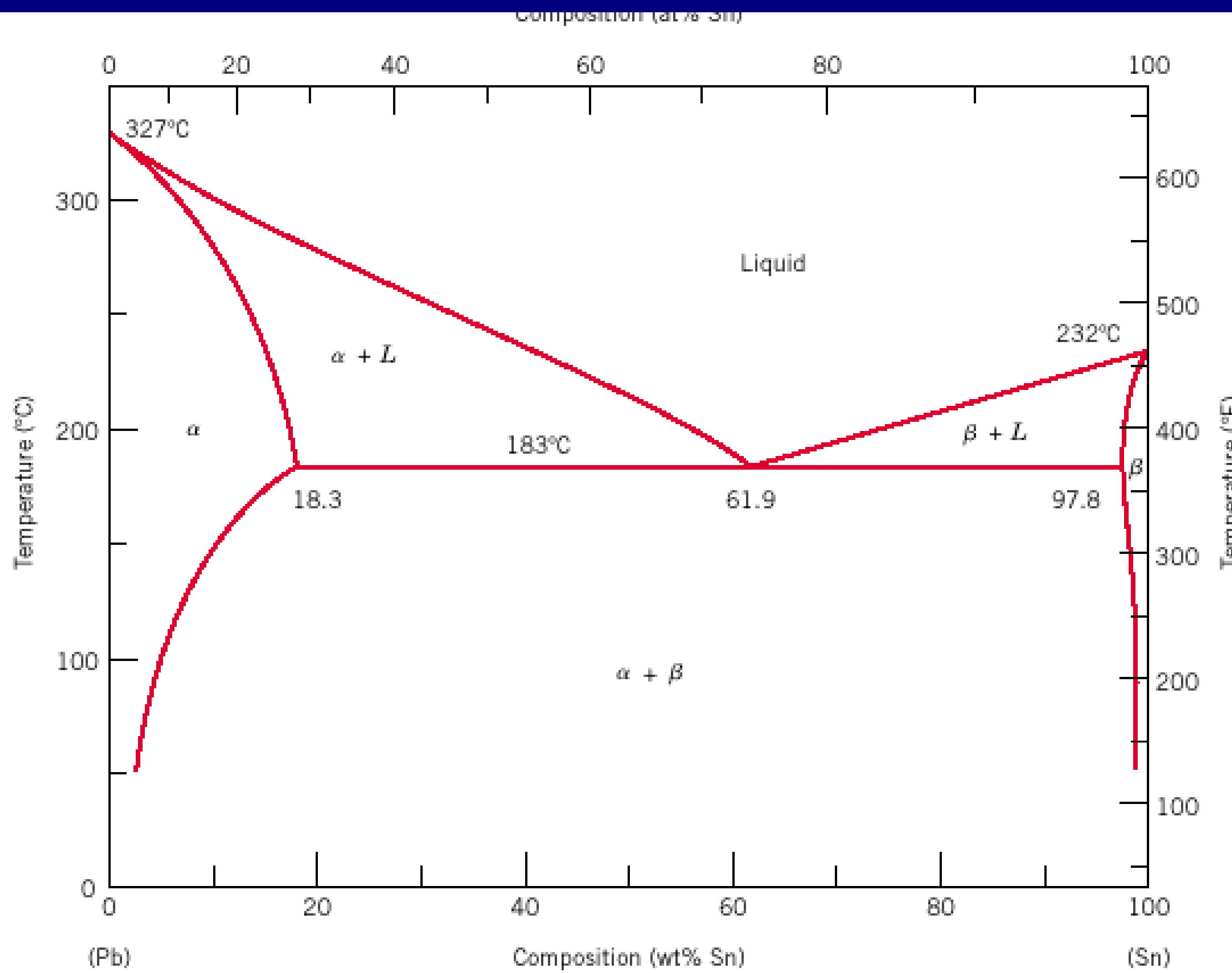


This is a fairly complex phase diagram; fortunately, most of the technologically interesting materials exist near the lower left-hand corner of the diagram.

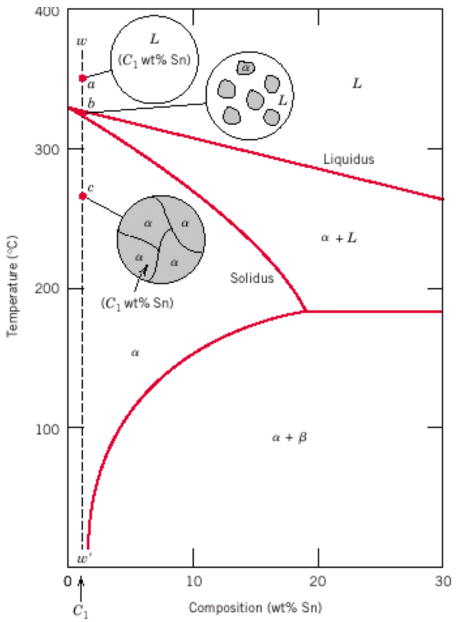
Binary systems: Ag-Cu

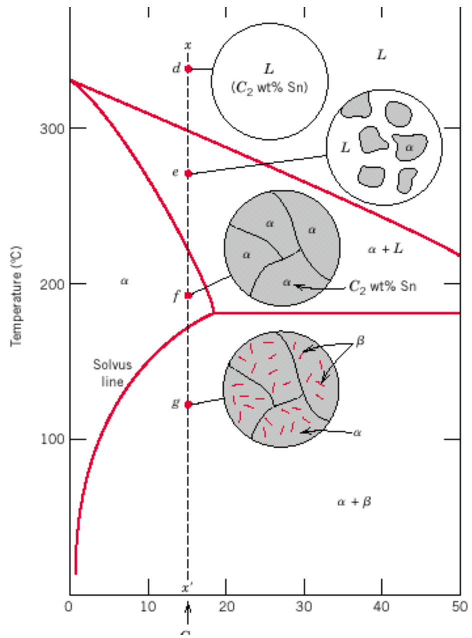


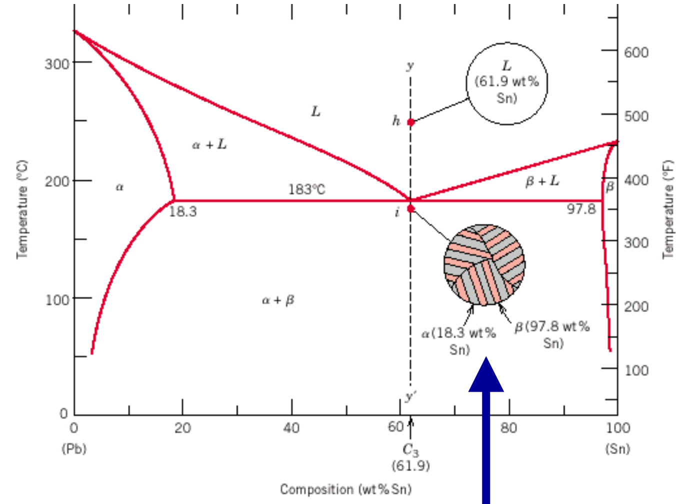
Binary systems: Pb-Sn

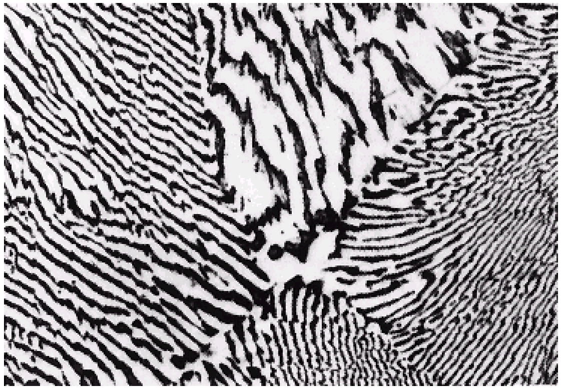


Binary systems: Pb-Sn microstructures





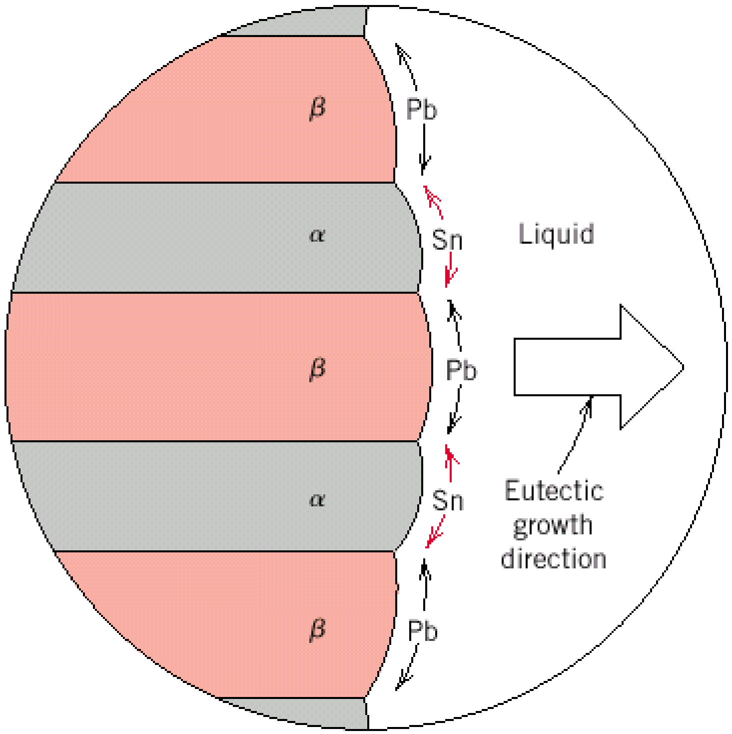


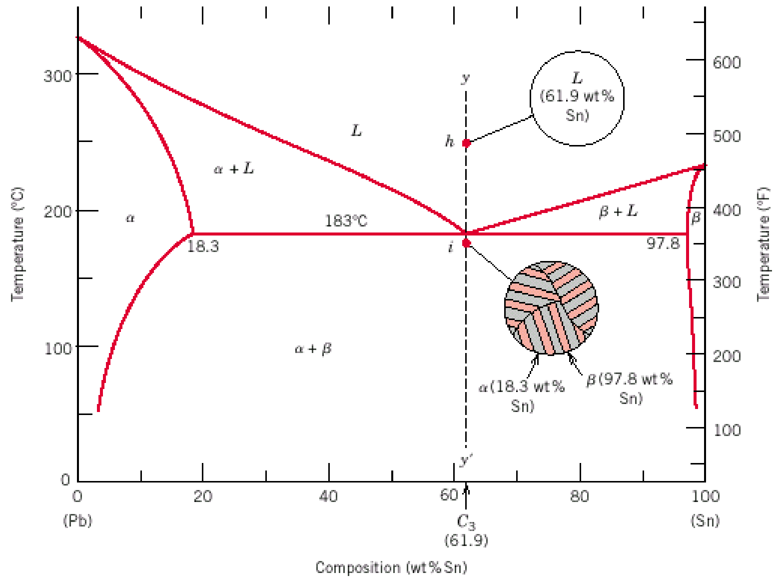


A eutectic microstructure

note the alternating light and dark bands in each grain.

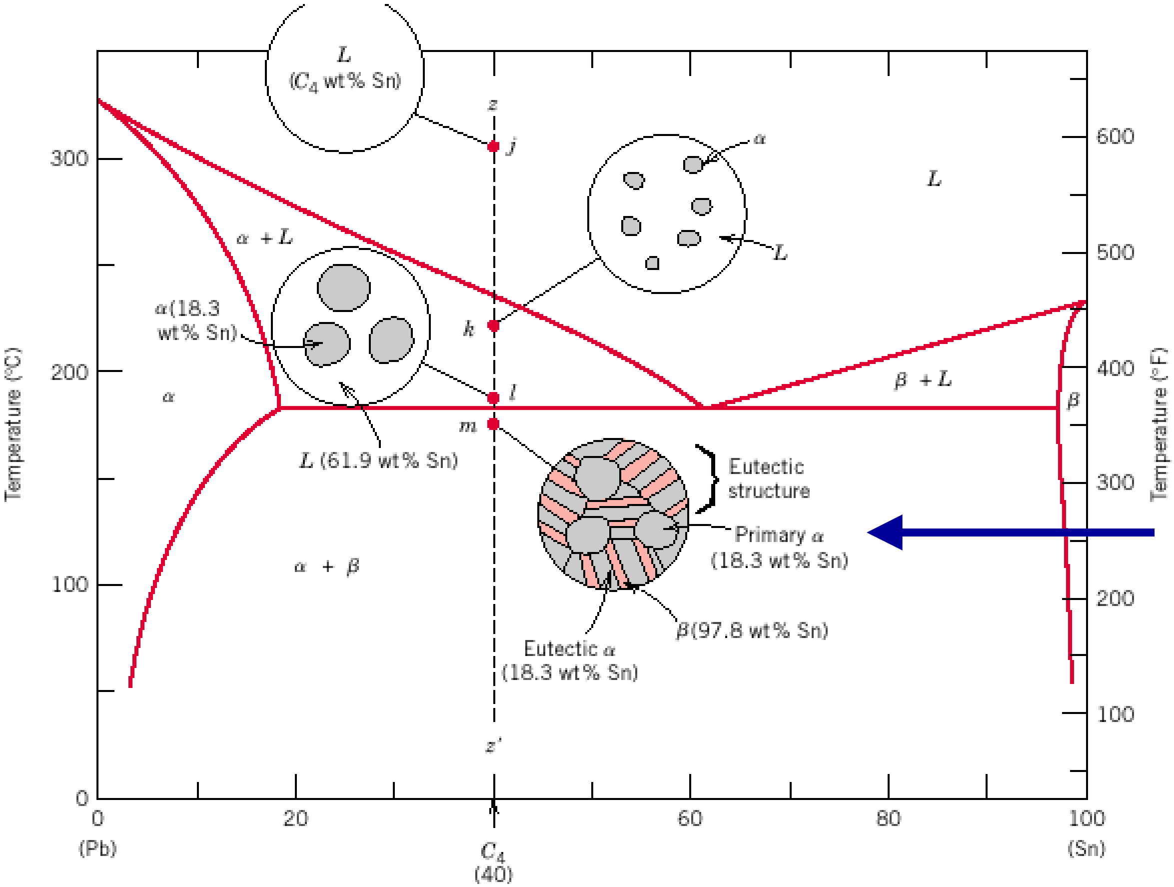
Binary systems: eutectic solidification

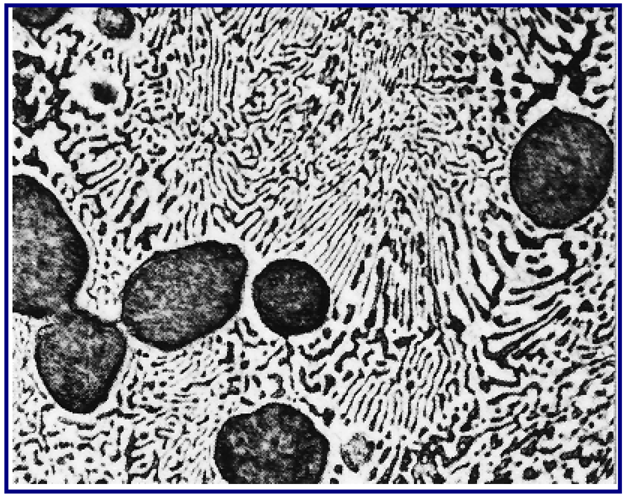




Eutectic microstructure

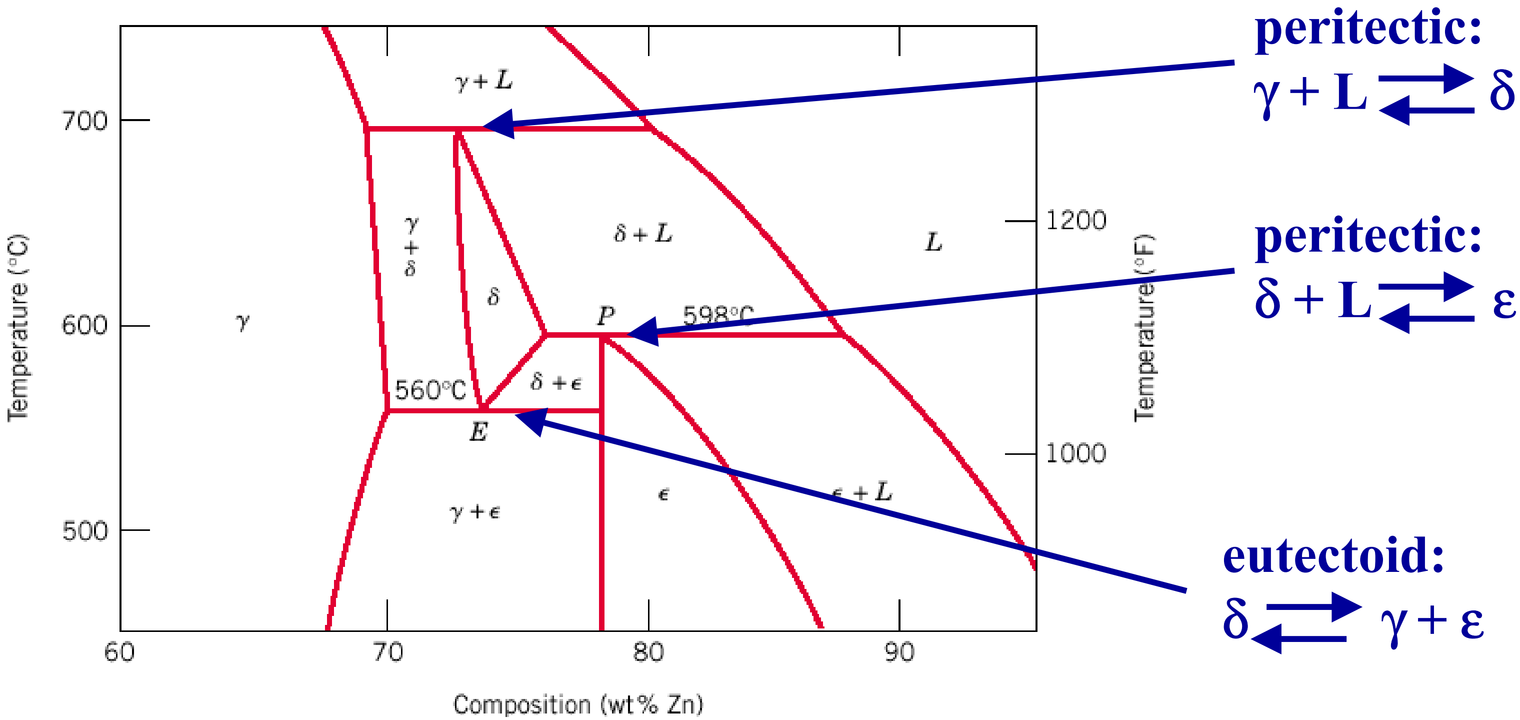
Binary systems: hypo-eutectic microstructures





Photomicrograph of a hypo-eutectic microstructure

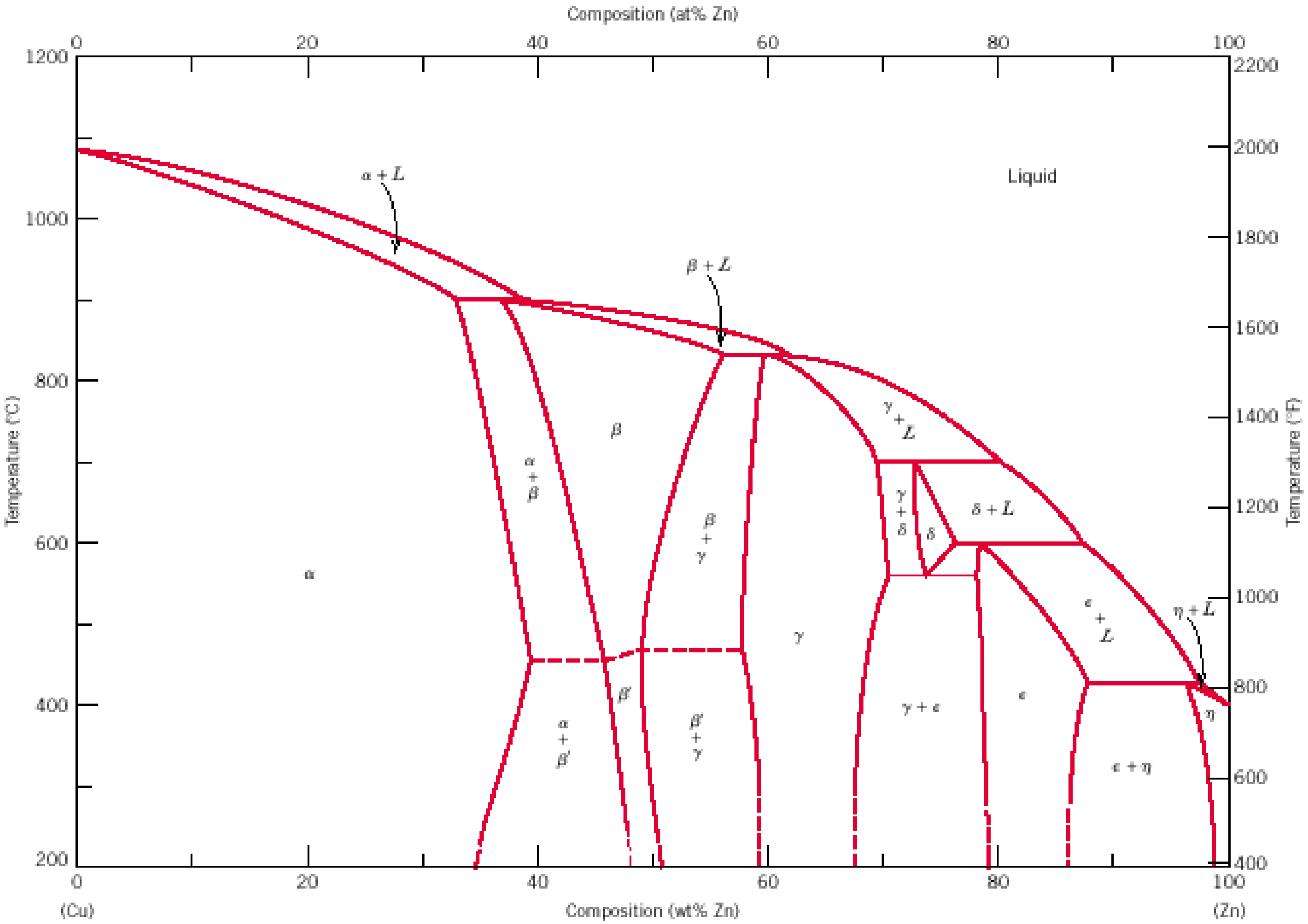
Binary systems: other invariant points



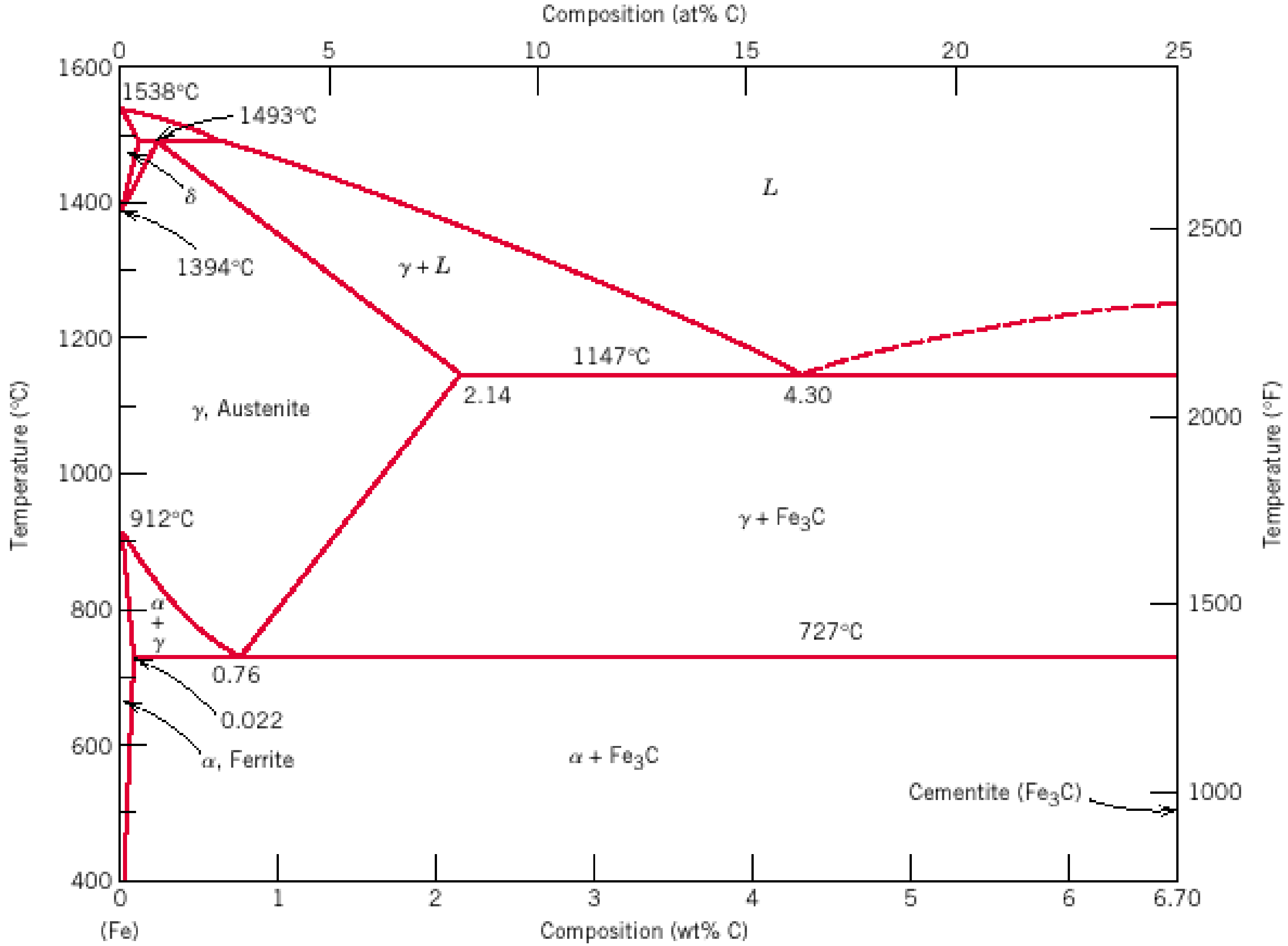
Eutectoid: one solid phase transforms into two other solid phases upon cooling

Peritectic: one solid and one liquid phase transform into another solid phase upon cooling

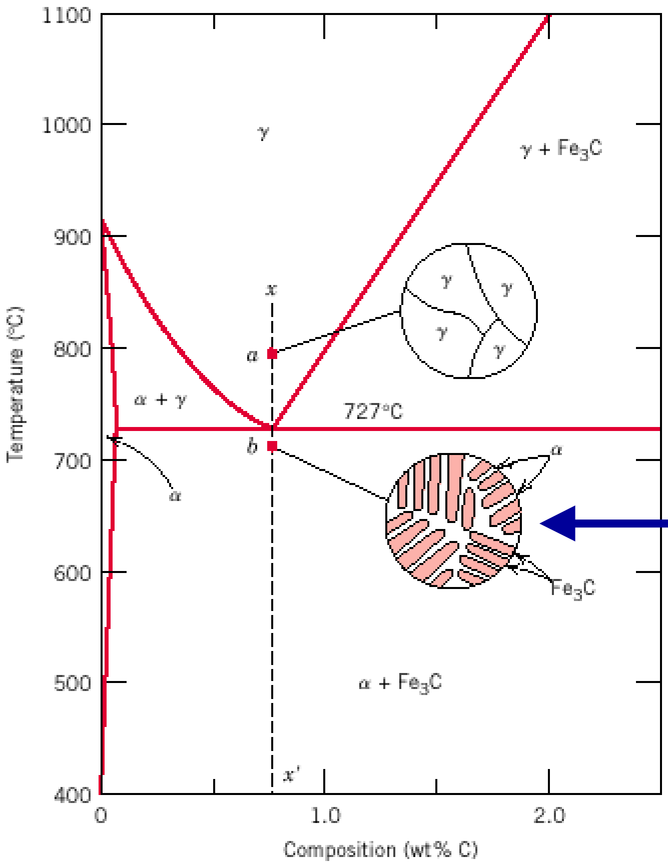
Intermediate phases: the Cu-Zn system

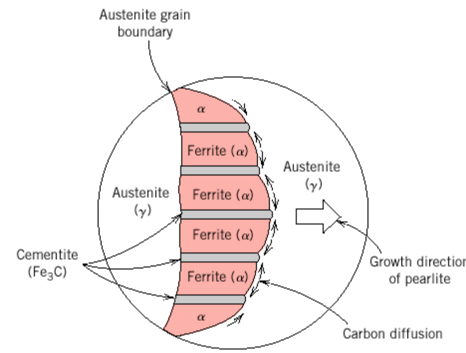


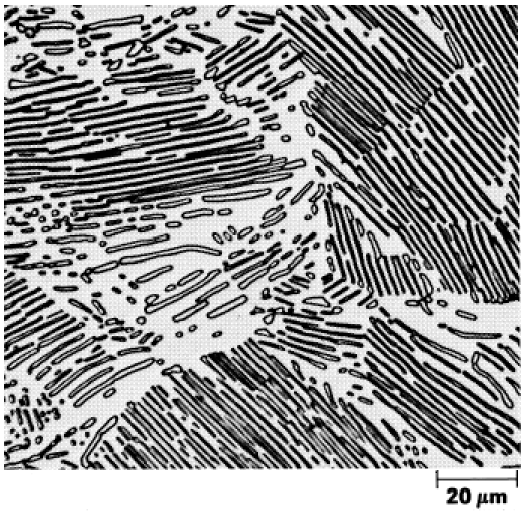
The Fe-C system



The Fe-C system: eutectoid microstructure

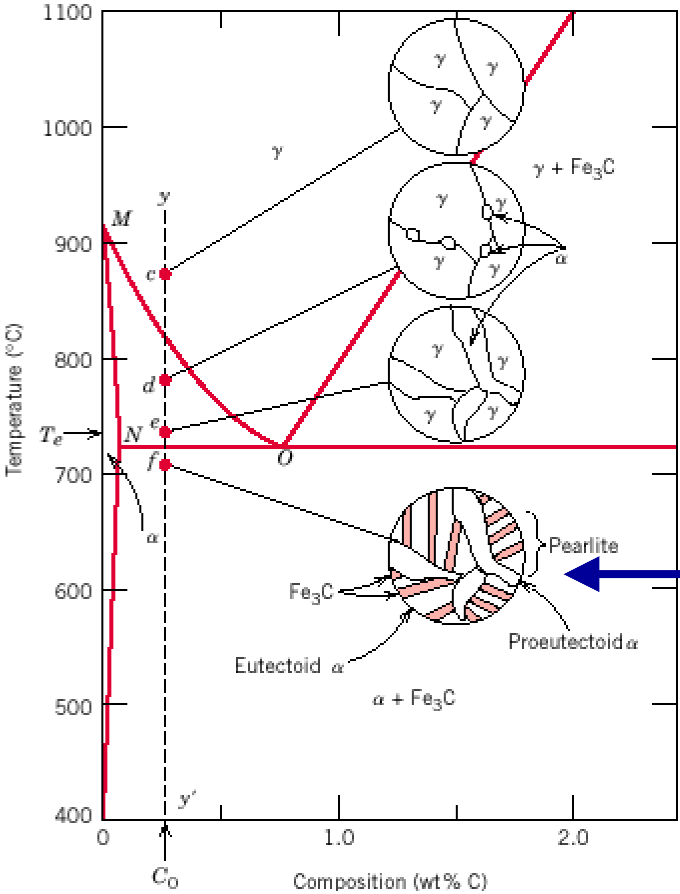


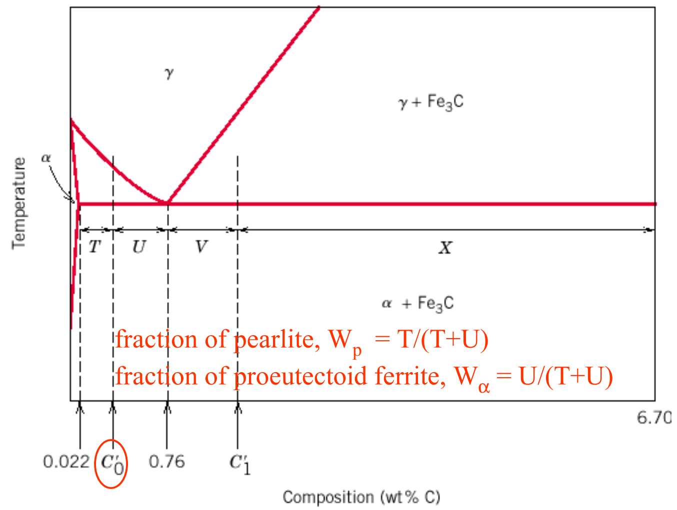


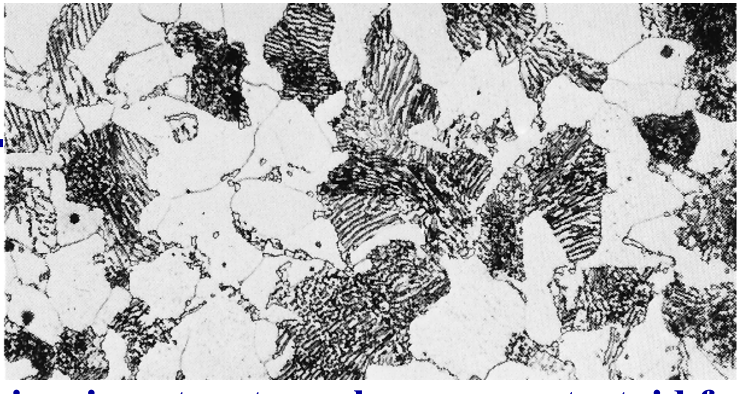


This microstructure is called "pearlite," which is a mixture of ferrite (α-Fe) + cementite (Fe_3C) (ferrite = light phase, cementite = dark phase)

The Fe-C system: hypo-eutectoid microstructure

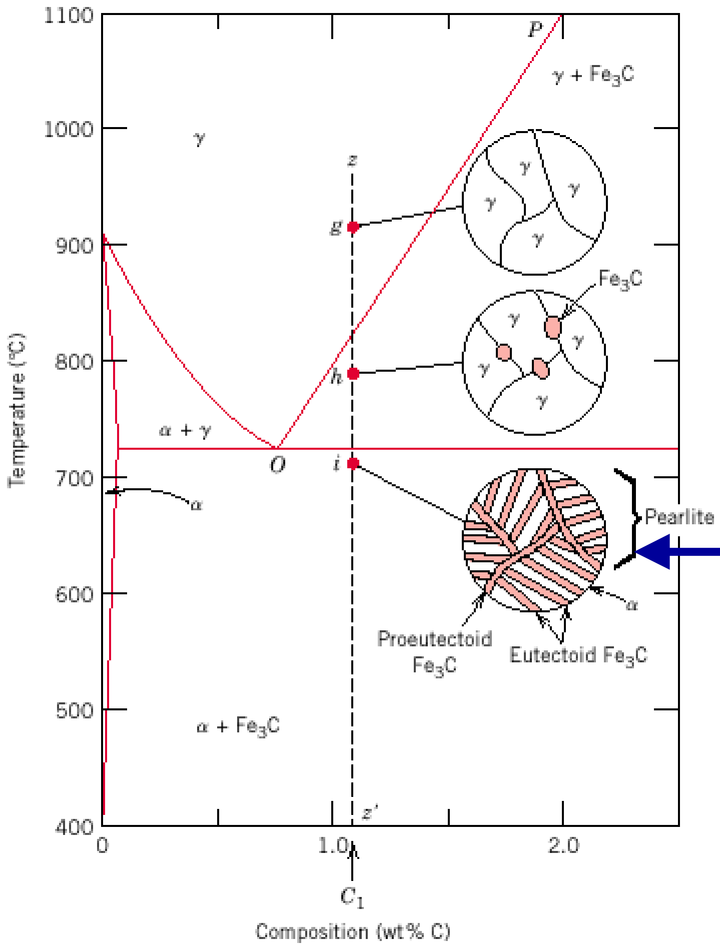


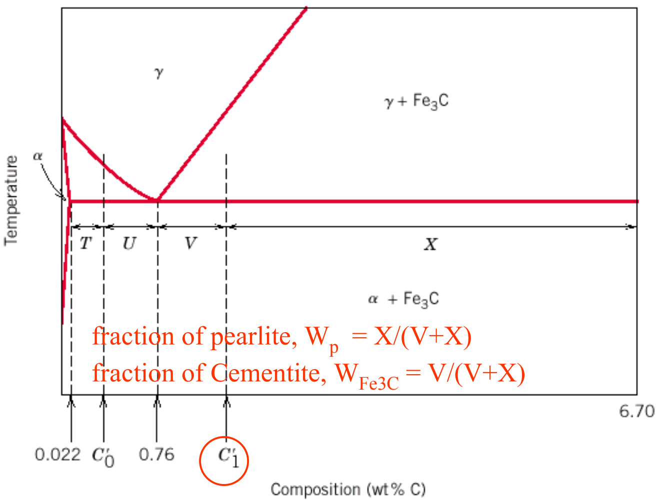




This microstructure shows proeutectoid ferrite and pearlite

The Fe-C system: hyper-eutectoid microstructure





This microstructure shows ferrite and proeutectic cementite