ENGINEERING COUNCIL

CERTIFICATE LEVEL

ENGINEERING MATERIALS C102

TUTORIAL 3 – THERMAL EQUILIBRIUM (PHASE) DIAGRAMS

UNIT OUTCOMES

On successful completion of the unit the candidate will be able to:

1. Recognise the structures of metals, polymers and ceramic materials.
2. Assess the mechanical and physical properties of engineering materials
3. Understand the relationships between the structure of a material and its properties.
4. Select materials for specific engineering applications.

If you intend to follow a career that involves the teaching or application of materials technology, especially metallurgy, a good understanding of phase diagrams is essential. The subject is not an easy one and this tutorial is designed to help students get started on the learning curve. This tutorial explains how materials arrange themselves when mixed and it is confined to Binary cases – two materials together. You will find many links to web sites carrying further descriptions and animated models that you should view to help with your understanding.

CONTENTS

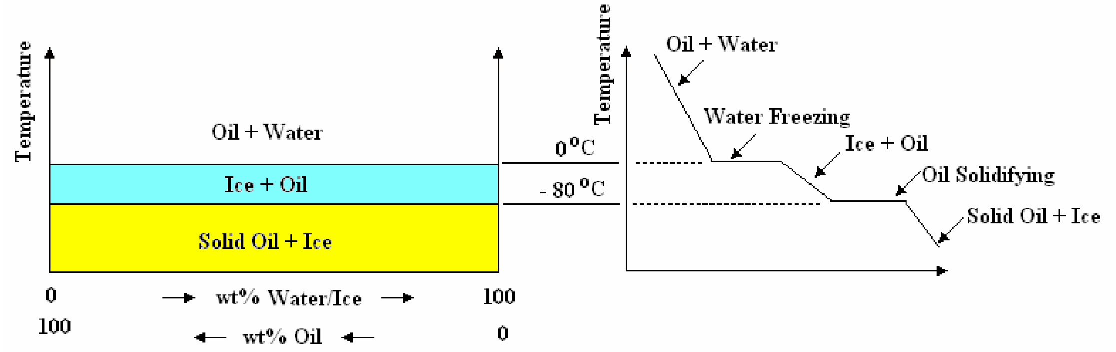
You will find good animated tutorials on this subject at

http://www-g.eng.cam.ac.uk/mmg/teaching/phasediagrams/index4.html
and
http://www.soton.ac.uk/~pasr1/steels.htm#page1

INTRODUCTION

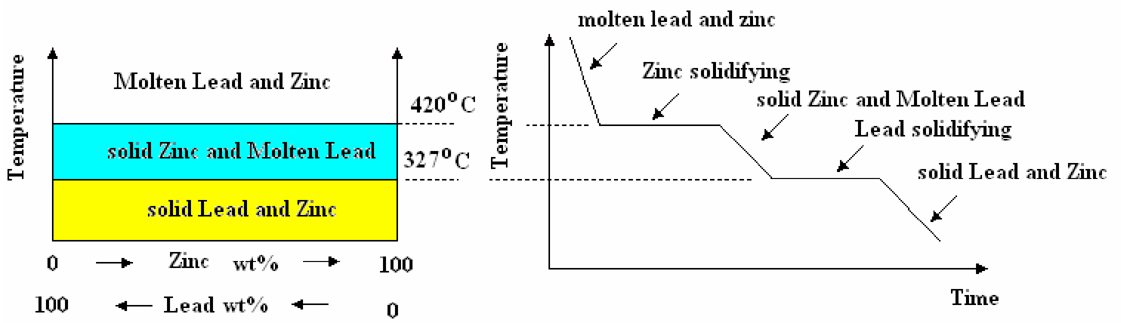
PHASE DIAGRAMS are graphical representations of the physical state or composition of two or more substances at various temperatures and various compositions. In metallurgy, they are particularly useful for finding the temperatures required to bring about structural changes in the solid. This is the science of heat treatment which is an important part of materials technology.

The simplest case to represent is that of two substances such as oil and water that will not dissolve when liquid or solid. Phase diagrams are produced by cooling the mixture at a constant rate and noting the pause in temperature when solidification takes place. First the water freezes at 0°C and then the oil typically at -80°C. This pause is due to the latent heat of fusion being given out and arresting the fall in temperature until the substance has entirely solidified. (The oil may not freeze as clearly as shown but the temperature is chosen to make the point).
The three **PHASES** are (oil + water), (Ice + oil) and (solid oil + ice). These are all double phases because the mixture at all times is two separate homogenous substances.
The **TEMPERATURE - TIME** graph will show the same two temperatures regardless of the quantities of each so the phase diagram will show the two boundaries separating the three phases as constant temperature lines.



The phase diagram shows us the structure (form) of the two substances at any temperature and any composition and clearly this is the same for all compositions. The composition is always shown as wt% which is defined as the weight of the given substance as a % of the total weight.

Another example is Lead and Zinc which will not dissolve in the liquid or solid state.



When one substance dissolves in the other, we have a new homogenous structure and the phase diagram becomes more complex. This is what we need to study and to understand it we need to understand solubility.

SOLUBILITY

The reasons why one substance will dissolve into another is not explained in any depth here. The substance being dissolved is called the **SOLUTE** and the substance into which it dissolves is called the **SOLVENT**. The more soluble the substance, the more it is capable of being dissolved. The solubility generally increases with temperature. What makes a substance soluble depends on its nature and in particular the size of the molecules. There is a maximum amount that will dissolve and when this point is reached the solvent is **SATURATED** with the solute. This may apply to a liquid or a solid.

LIQUID – LIQUID SOLUTIONS

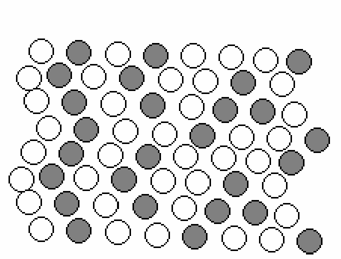
A liquid may or may not dissolve in another liquid. When oil and water are mixed, the oil will not dissolve in the water but when alcohol and water are mixed, the alcohol will dissolve into the water. The same is true of molten metals. For example, molten lead and molten zinc will not dissolve and when cooled to a solid, they will form two separate layers. On the other hand molten lead and tin will dissolve and form more complex structures when solidified.

SOLID – LIQUID AND LIQUID – SOLID SOLUTIONS

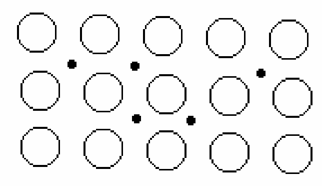
When a solid dissolves in a liquid, the molecules of the solid separate and become spaced between the molecules of the liquid. Salt and sugar will dissolve in water but sand will not. Sand is not soluble. Salt is dissolved by being broken up into two ions of sodium (Na) and Chlorine (Cl_2) which are attracted to the water molecule. Go to this link for a video clip of this.
http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/molvie1.swf

Liquid will also dissolve into a solid as when we have damp salt or damp sugar.

SOLID – SOLID SOLUTIONS



Sometimes the two substances will dissolve and remain dissolved when solidified such as carbon and iron or copper and aluminium. This is called a SOLID SOLUTION. This is most likely with metals when they have similar properties with atoms that are approximately of equal size as shown.



A solid solution will also form when the molecules of one are so small that it fits into the spaces between the larger molecules (called the interstitial spaces). This is what happens with carbon and iron.

Sometimes both metals will dissolve in each other such as with Lead and Tin. When lead is the major part, the tin dissolves in it. When tin is the major part, the lead dissolves in it.

Substances like salt and water will not dissolve when both are solid. Let's now see how to explain the phase diagram for salt and water.

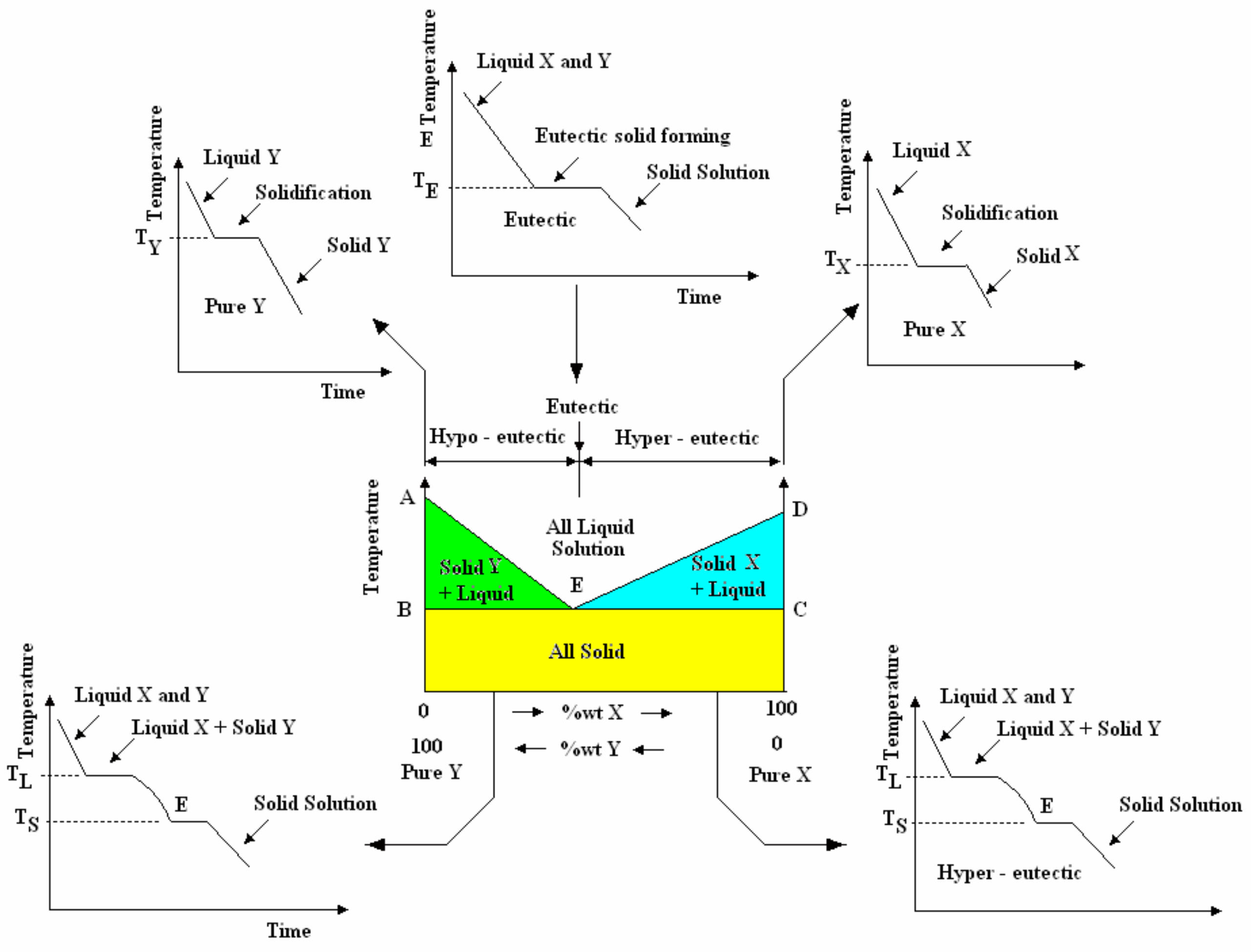
Let's go back to studying phase diagrams this time for the cases where the two metals are mutually soluble as solids.

SIMPLIFIED PHASE DIAGRAM for BINARY EUTECTIC ALLOYS

Consider two metals X and Y that are mutually soluble. The pure metal Y on the left solidifies at its melting point T_Y. The pure metal X on the right solidifies at its melting point T_X. In between the two extremes the temperature at which solidification starts is lower because of the affect of one being dissolved in the other. This temperature is denoted T_L because only liquid exists above this temperature. The temperature at which the solution becomes completely solid is denoted T_S because below this temperature we only have solid. The cooling curves are shown for the various contents.

The green region is called **HYPO – EUTECTIC** and contains solid pure Y and a saturated liquid solution.
The blue region is called **HYPER – EUTECTIC** and contains solid pure X and a saturated liquid solution.
At point E we have a very special case where both X and Y are saturated liquids and only one solidification temperature called the eutectic temperature T_E. It follows that the T_S is the same as T_E in all cases because as one metal solidifies, the remaining liquid solution becomes richer in the other until the liquid reaches the eutectic composition. These types of binary alloys with a eutectic point are called **EUTECTIC ALLOYS.**

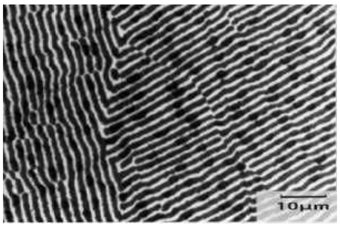
Above the line A E D everything is liquid and this line is called the ***LIQUIDUS***.
Everything below the line B E C is solid and this line is called the ***SOLIDUS***.
Point E is called the ***EUTECTIC*** point.



Clearly the diagram is not complete because at point B we have pure Y and so immediately below point B we must have solid Y. Similarly immediately below point D we must have solid X. The solidus cannot be quite as shown and this is covered a little later. First let's look at the microstructure of the solids formed.

EUTECTIC STRUCTURE

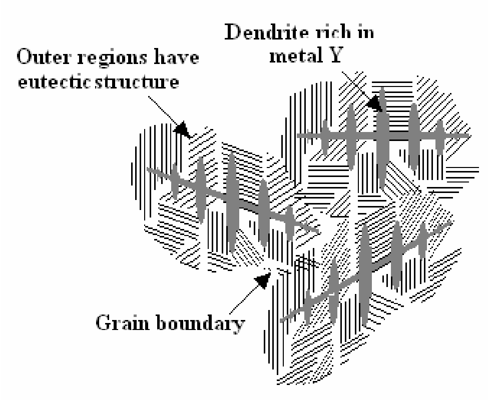
Consider what happens when we cool a molten solution containing the exact eutectic ratio of the two metals X and Y. The molten solution cools until Y starts to solidify. As soon as this happens the remaining liquid becomes rich in metal X and that metal will start to solidify. The liquid then becomes rich in metal Y and this will solidify and so the process will go on with the two metals forming solid laminar layers of pure metal X and Y. All this will happen at one temperature – the eutectic temperature and the cooling curve will resemble that of a pure metal. The structure is the eutectic structure.



HYPO – EUTECTIC STRUCTURE

Consider what happens when a liquid solution to the left of E is cooled down. As the material solidifies, crystals of metal Y form as a dendrite as shown. This is a pattern like that of a snowflake.

The remaining liquid becomes richer in metal X and at some point the liquid will have a composition corresponding to point E. Further cooling produces a eutectic structure so we have dendrite crystals of Y in a eutectic matrix.



HYPER EUTECTIC STRUCTURE

If we start to the right of E the same process occurs but this time we have dendrites of pure X in a eutectic matrix.

The simplified phase diagram explained so does not have perfect straight lines A E D but the exact path of these lines is not important and does not affect the final solid structure.

The main inaccuracy of the phase diagram is that it does not show the affect of solid solution explains this addition to the phase diagram. A good example of this is Lead and Tin so we will use this as a case study and bring in a new boundary called the SOLVUS.

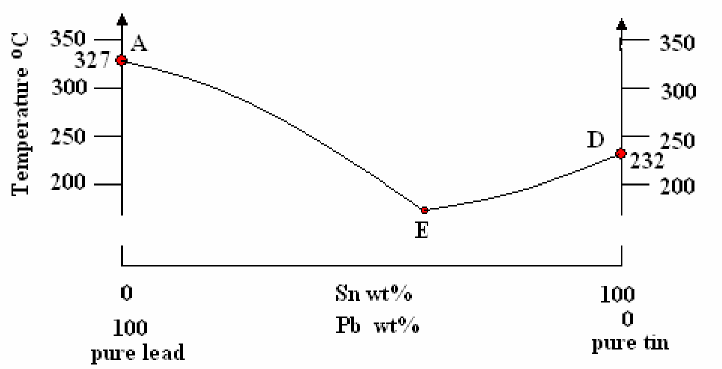
CASE STUDY LEAD – TIN

You will find good descriptions of phase diagrams at the following web sites.

http://www.chemguide.co.uk/physical/phaseeqia/snpb.html

http://www.soton.ac.uk/~pasr1/index.htm

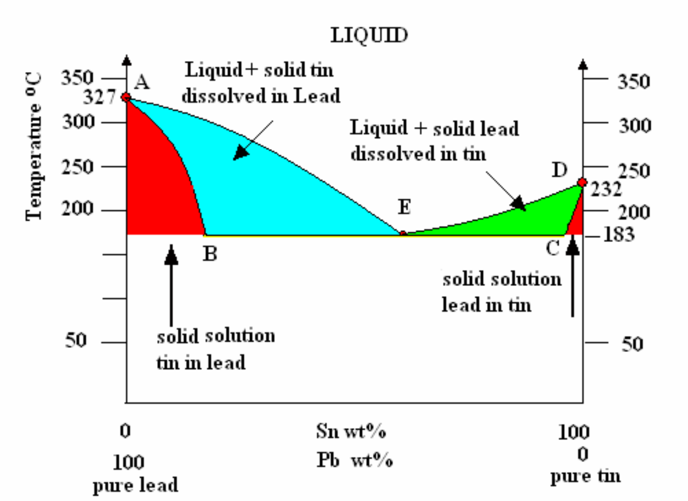
Lead and tin are mutually soluble when both are liquids. The presence of one in the other depresses the melting temperature and the solidus is as shown. Note that we are not very interested in the composition when both are liquid so the saturation points are not drawn for this region. The points of interest are the melting points for various solutions.



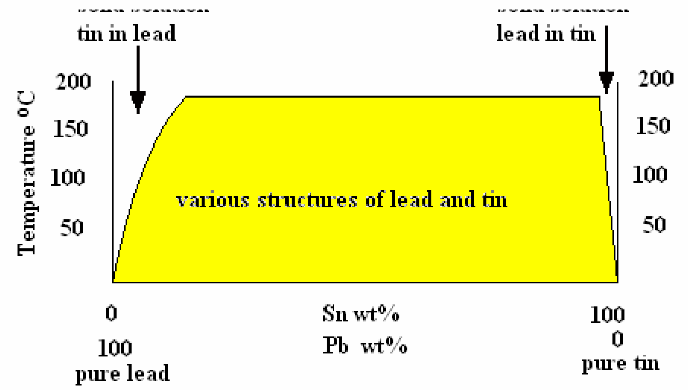
Point A is the melting point of pure lead and point D is the melting point of pure tin. E is the Eutectic point where they meet. Anything above the line is a liquid and the line is called the LIQUIDUS.

Immediately below point below point A we must have solid lead and immediately below point D we must have solid tin. There must be a region on both sides representing the unsaturated solid solution and the solidus takes the path A B E C D. The red regions are solid solutions. AB and CD show the points where the solid solution is saturated. The blue region is a saturated liquid with solid lead. The green region is saturated liquid and solid tin.

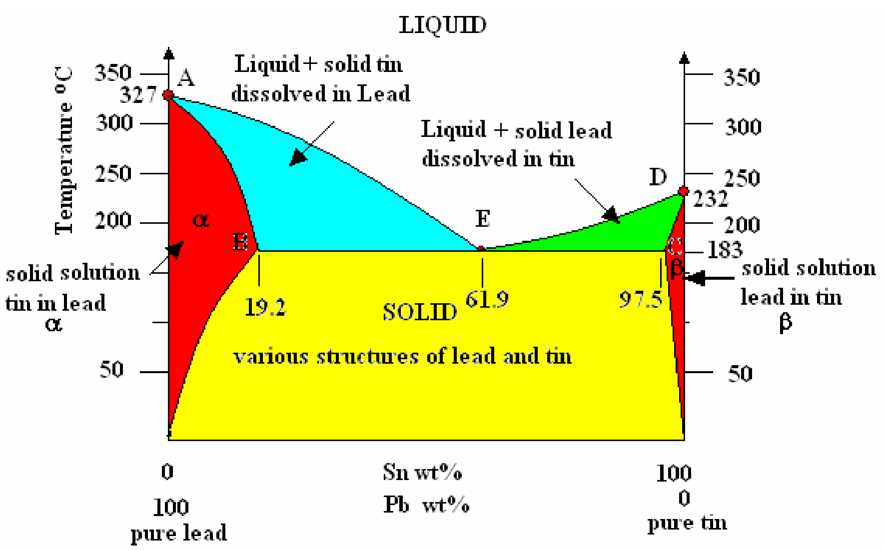
The diagram now shows the correct solidus. At the extreme left we have a solid solution of tin in lead and at the extreme right we a solid solution of lead in tin.



Lead and tin are mutually soluble when solid. Just as with solids in liquids, a solid – solid solution will have two saturation points that change with temperature. This gives the diagram shown. The yellow region is the saturated solid with either tin or lead.



To complete the picture we bring the two halves of the diagram together



The line AED is the **LIQUIDUS** and the line ABECD is the **SOLIDUS**. The two red regions are where we have unsaturated solid solutions. In general for any eutectoid, these regions are called the ALPHA (α) and BETA (β) phases. The boundary of the red regions is called the **SOLVUS**.

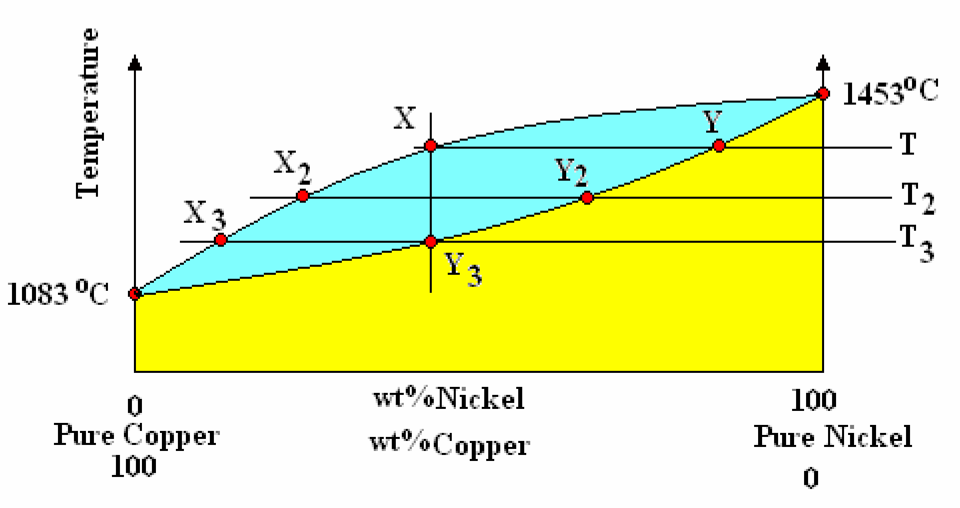
The microstructure in the red regions is of a uniform solid solution.

You will find a good explanation of phase diagrams at this web site.
http://www.soton.ac.uk/~pasr1/build.htm#page1 and at
http://www.doitpoms.ac.uk/tlplib/phase-diagrams/printall.php

There are cases of binary alloys that have no eutectic point such as Nickel and Copper and this is discussed next.

CASE STUDY NICKEL – COPPER ALLOY

Nickel and copper have similar size molecules and both form a FCC crystal lattice. The equilibrium diagram is shown below. This alloy has long been used for making coins. The alloy is unusual because both metals are completely soluble in the other at all compositions so there never a saturated liquid and no eutectic point.



The melting points of pure nickel and copper are 1453°C and 1083°C respectively. Because they are soluble in both states, the diagram consists of only two lines, the solidus and liquidus. In between the substance is a pasty solution.

The molten alloy starts off as a uniform liquid solution. When cooled slowly to temperature T on the liquidus line we have a liquid of composition X and a solid of composition Y. Further cooling to temperature T_2 produces a liquid of composition X_2 and a solid of composition Y_2. In this condition the dendrites are forming with a uniform structure in a liquid of uniform structure. Cooling produces a liquid with less and less nickel and a solid with more and more copper. Finally the whole structure is solid at temperature T_3.

Because of the similar size of the molecules and crystalline structure, the molecules can rearrange themselves in the solid state, a process called diffusion. Because of this the solid becomes a uniform solid solution with a composition Y_3.

SELF ASSESSMENT EXERCISE No.1

1. Explain the meaning of the following terms.

   Uniform solid solution.
   Saturated solid solution.
   Eutectoid.
   Dendrite.
   Hyper-eutectic.
   Hypo-eutectic.
   Solidus.
   Liquidus.

2. Explain with diagrams the microstructure of the following.

   A Eutectic structure.
   A hyper – eutectic structure of Lead and Tin.
   Solid solution of Copper and Nickel.

3. Construct an accurate bismuth-tin phase diagram using percentage by weight (wt%) of tin on the composition axis using the following information.

   It is a EUTECTIC system

   The melting point of pure bismuth is 271°C

   The melting point of pure tin is 232°C

   The eutectic temperature is 138°C

   The eutectic composition is 43wt% Sn and 57wt% Bi

   The maximum solubility of tin in bismuth is 4wt% at the eutectic temperature and falls to zero at 50°C

   The maximum solubility of bismuth in tin is 21wt% at the eutectic temperature and falls to 3wt% at room temperature.

4. Using the information for Q1, describe the microstructural evolution that takes place as a sample containing 60wt% Sn is slowly cooled from 250°C to room temperature. What will be the effect of increasing the cooling rate?

5. Using the same information again, calculate for the 60wt% Sn alloy, the weight fraction of a (bismuth-rich) and β (tin-rich) solid solution that co-exists when the temperature is 100 °C, assuming the relevant phase boundaries are straight lines.

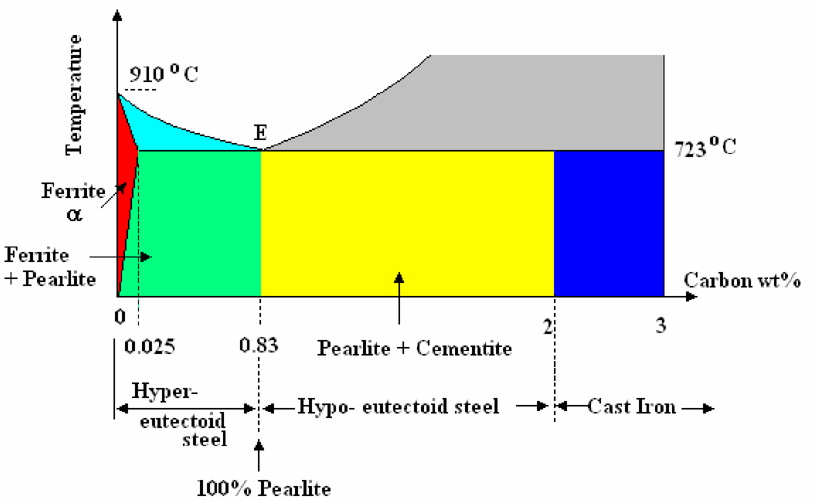
IRON – CARBON PHASE DIAGRAM

One of the most important materials in engineering is iron used as a base for many alloys. The most important alloys are iron and carbon steel. Carbon dramatically affects the properties of iron producing a range of strengths, ductility and hardness. Many other materials are used to produce alloys of iron but this section will only deal with iron and carbon.

The complete phase diagram is very complex. Matters are further complicated because pure iron exists in different crystalline forms (allotropies).
Below 910°C it a body centres cubic crystal (BCC) called **ALPHA IRON** (α).
Between 910°C and 1403°C iron exists as faced centre cubic crystal (FCC) called **GAMMA IRON** (γ). This is non magnetic iron.
Between 1403°C and the melting point of iron 1535°C, the iron exists as a body centred cubic crystal called **DELTA IRON** (δ).

Matters are further complicated because iron and carbon will combine chemically to form ***IRON CARBIDE*** (Fe_3C). This is also called ***CEMENTITE***. It is white, very hard and brittle. Much of the content is about a solution of cementite rather than pure iron hence extra phases are introduced. The many and varied microstructures of iron and carbon give rise to many names to describe them and some will be given in the following text. Let's start by just examining the solid region below the eutectic 723°C.

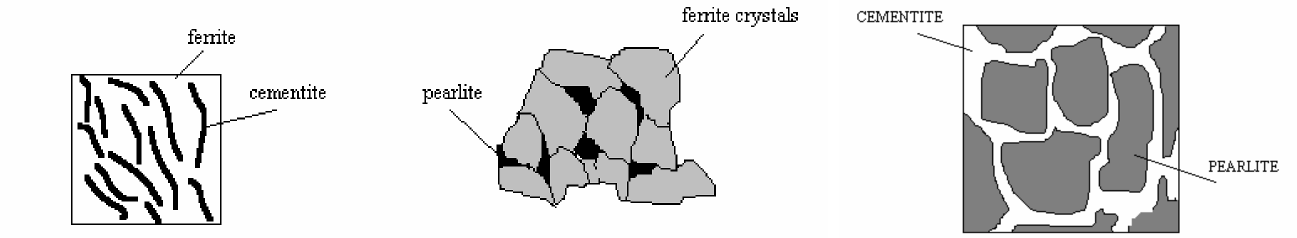
In the red region we have the alpha (α) phase. This is an unsaturated solid solution of iron and carbon called **FERRITE**. The iron in this phase is a body centres cubic crystal (BCC). The magnetic properties of this material are of particular importance.



The green region contains hyper-eutectic steel commonly called mild steel. This is a solution of 87% ferrite and 13% cementite called **PEARLITE**. The microstructure is shown below.

The eutectic temperature is 723°C and the eutectic composition is 0.83 wt% Carbon. The eutectic structure is entirely pearlite.

The yellow region contains hypo-eutectic steel commonly called high carbon steel. This is a structure of Pearlite and Cementite.



THE STRUCTURE OF PEARLITE   THE STRUCTURE OF MEDIUM CARBON STEEL   THE STRUCTURE OF HIGH CARBON STEEL

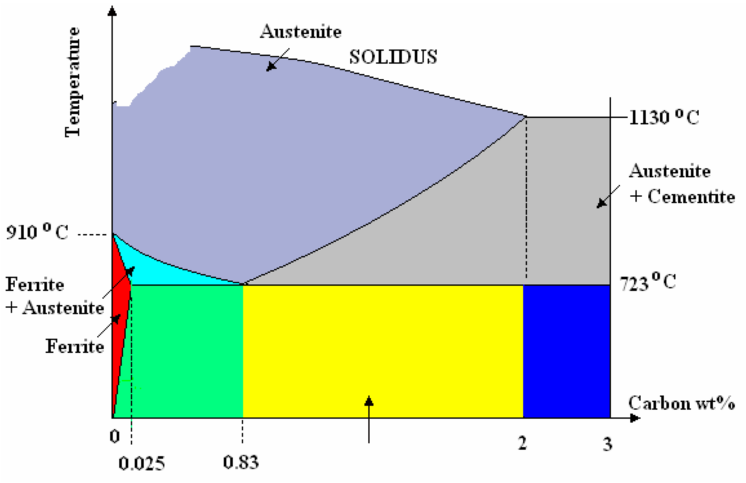
At higher quantities of carbon, the carbon starts to appear as free graphite and we have what is commonly called **CAST IRON**.

Now let's examine the upper regions of the diagram.

The Region indicated as Austenite contains a solid solution of gamma iron with carbon or cementite. Clearly this only exists when the steel is very hot and must change to another structure when cooled.

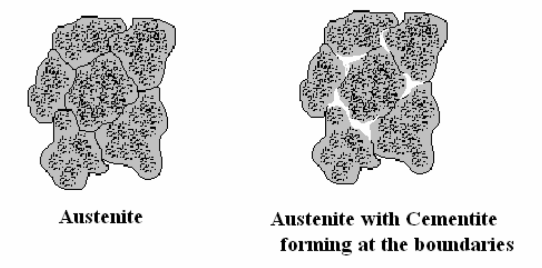
The next tutorial discusses what happens when it is cooled very quickly.

The grey region indicated contains a mixture of austenite and cementite.

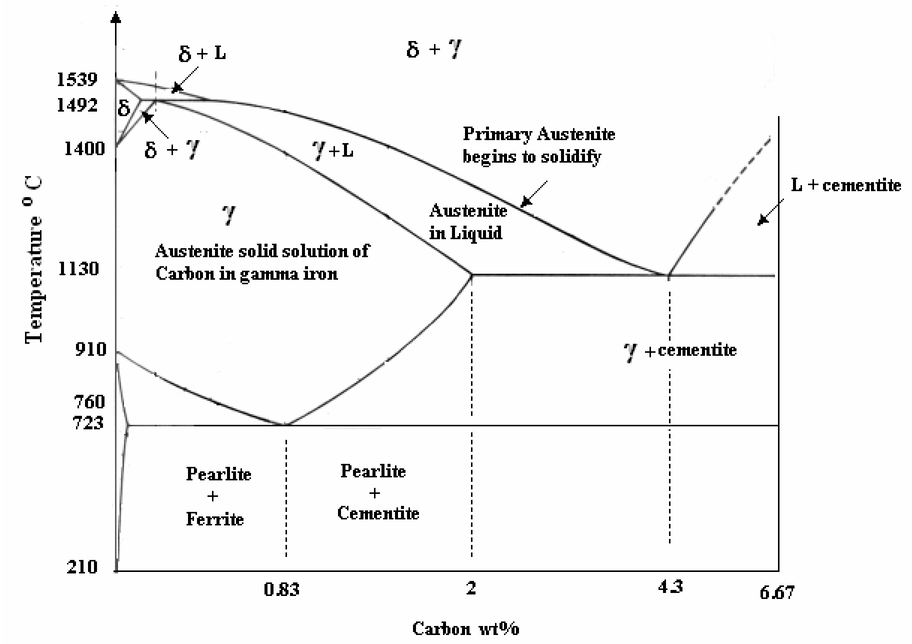


Note that we have a second eutectic point at 2%C and 1130°C.

The microstructures are like this.



Above these regions we have liquid apart from the area where delta iron produces yet another set of phases but this is not discussed here. This is as far as the discussion goes here but the complete phase diagram is shown next for reference.



Useful web sites on this topic are:

http://www.ul.ie/~walshem/fyp/iron%20section.htm
http://www-g.eng.cam.ac.uk/mmg/teaching/typd/addenda/eutectoidmicrostructure1.html
http://www.sv.vt.edu/classes/MSE2094_NoteBook/96ClassProj/examples/kimcon.html

SELF ASSESSMENT EXERCISE No.2

1. Explain the meaning of the following terms.

   Ferrite
   Cementite
   Austenite
   Pearlite
   Gamma Iron
   Alpha Iron
   Delta iron

2. Sketch the microstructure of a 0.2 wt % carbon steel.

3. Sketch the microstructure of a 1.2 wt% carbon steel.