EDEXCEL NATIONAL CERTIFICATE

UNIT 10: PROPERTIES AND APPLICATIONS OF ENGINEERING MATERIALS

NQF LEVEL 3

OUTCOME 1 - TUTORIAL 2
PHASE EQUILIBRIUM DIAGRAMS

Unit content

1 Be able to describe the structure of and classify engineering materials

Atomic structure: element; atom e.g. nucleus, electron; compound; molecule; mixture; bonding mechanisms e.g. covalent, ionic, metallic

Structure of metals: lattice structure; grain structure; crystals; crystal growth; alloying e.g. interstitial, substitutional;

Phase equilibrium diagrams e.g. eutectic, solid solution, combination; intermetallic compounds

Structure of polymeric materials: monomer; polymer; polymer chains e.g. linear, branched, cross-linked; crystallinity; glass transition temperature

Structure of ceramics: amorphous; crystalline; bonded Structure of composites: particulate; fibrous; laminated

Structure of smart materials: crystalline; amorphous; metallic

Classification of metals: ferrous eg plain carbon steel, cast iron (grey, white, malleable, wrought iron), stainless and heat-resisting steels (austenitic, martensitic, ferritic); non-ferrous e.g. aluminium, copper, gold, lead, silver, titanium, zinc; non-ferrous alloys e.g. aluminium-copper heat treatable – wrought and cast, non-heat-treatable – wrought and cast, copper-zinc (brass), copper-tin (bronze), nickel-titanium alloy

Classification of non-metals (synthetic): thermoplastic polymeric materials e.g. acrylic, polytetrafluoroethylene (PTFE), polythene, polyvinyl chloride (PVC), nylon, polystyrene; thermosetting polymeric materials e.g. phenol-formaldehyde, melamine-formaldehyde, urea-formaldehyde; elastomers; ceramics e.g. glass, porcelain, cemented carbides; composites e.g. laminated, fibre reinforced (carbon fibre, glass reinforced plastic (GRP), concrete, particle reinforced, sintered; smart materials e.g. electro-rheostatic (ER) fluids, magneto-rheostatic (MR) fluids, piezoelectric crystals

Classification of non-metals (natural): e.g. wood, rubber, diamond

The topic covered here is a wide and difficult area of study and it is unlikely that the intention is for you to understand more than the basic elements. It is up to you and your tutors to decide how much you need to do.

THERMAL EQUILIBRIUM or PHASE DIAGRAMS

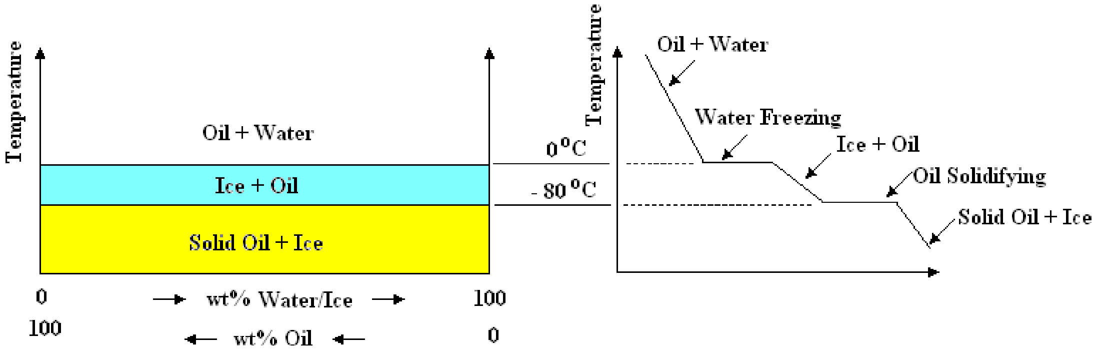
In tutorial 1 you learned that alloys are solutions of two or more materials. The structure formed by an alloy depends on the proportions it contains of each material. The structure is also affected by the temperature of the liquid or solid. The following is about a graphical representation of the various states of alloys and mixtures for various proportions at various temperatures. The resulting diagrams have varying degrees of complexity depending on the chemical compounds that forms and the solubility of each substance in the solid and liquid states.

CASE 1 – Both Substances Insoluble in Liquid and Solid State.

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).

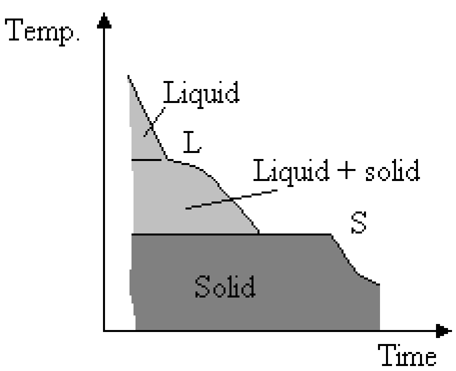
The three **PHASES** are (oil + water), (Ice + oil) and (solid oil + ice). These are all double phases because the mixture at all times is two separate homogenous substances.

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 same thing happens with two metals that are insoluble in both the liquid and solid state. As the molten solution is cooled, the metal with the higher melting point will solidify first and then the metal with lowest melting point. They will form separate layers of the pure material. This will happen regardless of the proportion of each metal.

CASE 2 - Substances are SOLUBLE as Liquids but not as Solids.



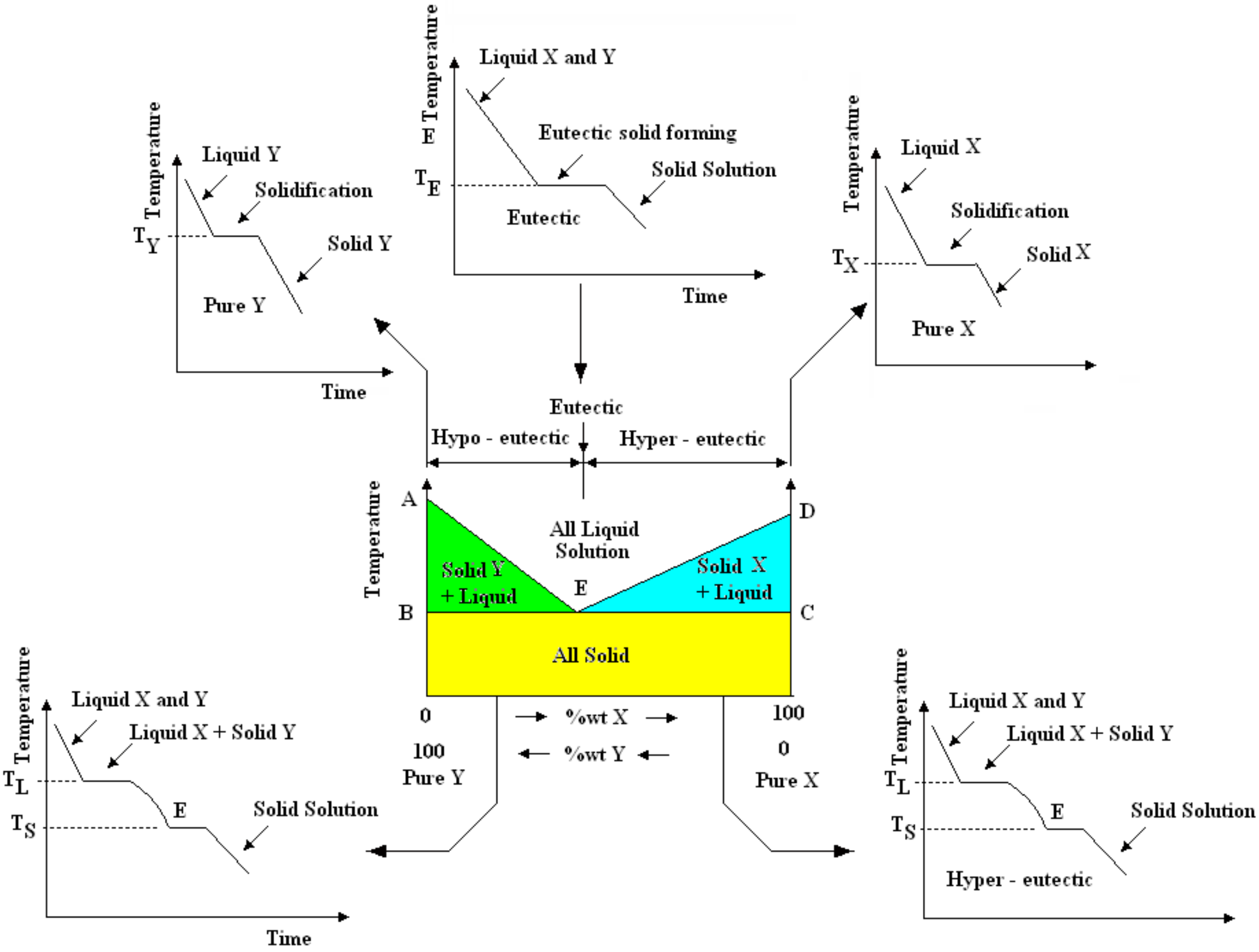
If we take a particular proportion and allow it to cool down from the liquid state we find that there are two pauses in the cooling rate at L and S.

L is the temperature at which solidification starts and S is the temperature at which it ends. These temperatures vary according the proportions of each metal.

The melting point is depressed when two substances are mixed (e.g. salty water freezes below 0° C). This is true of metals in solution so temperatures L and S are not the melting point of either metal except when it is 100% of one or the other. We can measure the temperatures at L and S for various proportions of two substances X and Y and plot them against the proportion (by weight).

The resulting diagram (in colour below) is the phase or equilibrium diagram.

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

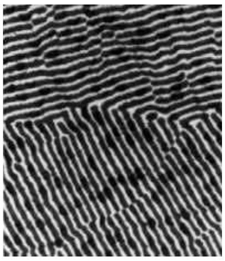


Consider what happens when a liquid solution to the left of E is cooled down. At some temperature metal Y starts to solidify and forms dendrite crystals. The remaining liquid becomes richer in metal X and at some point the liquid will have a composition corresponding to point E and in fact goes slightly to the right of E. At this point metal X starts to solidify but this then makes the composition move to the left of E. Metal Y then solidifies further and the composition swings back to the right of E and metal X solidifies. This continues until everything is solid. The resulting structure will be crystals of pure metal Y and a laminate structure of metals X and Y.

If we started to the right of E we would end up with pure metal X and a laminate structure.

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.

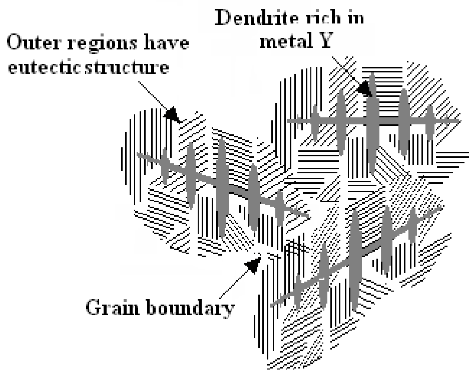
EUTECTIC STRUCTURE



Consider what happens when we cool a molten solution containing the exact eutectic ratio of the two metals X and Y (point E). 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.

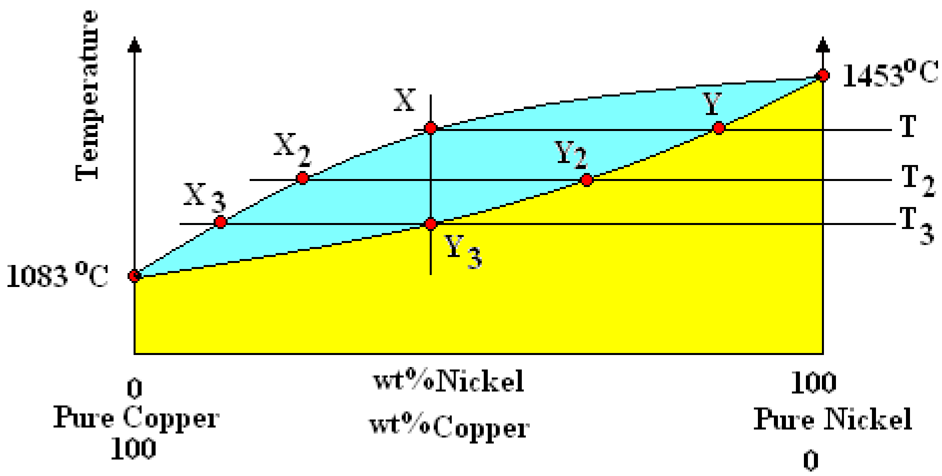
HYPER EUTECTIC STRUCTURE

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 far 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.

CASE 3 - Two Metals are Soluble Both in the Liquid and Solid State.

An example of this is nickel and copper that has 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 is 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.

THERMAL EQUILIBRIUM DIAGRAM FOR CARBON AND IRON

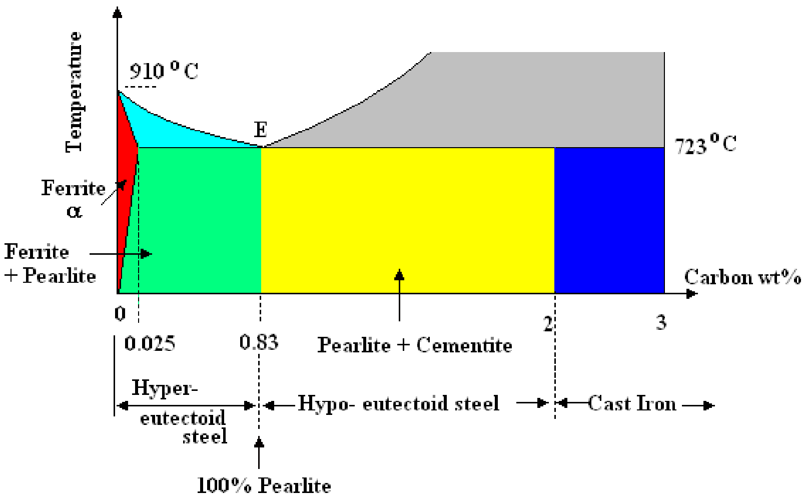
One of the most important materials in engineering is iron used as a base for many alloys. The most important alloys are iron and carbon steel. Carbon dramatically affects the properties of iron producing a range of strengths, ductility and hardness. Many other materials are used to produce alloys of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

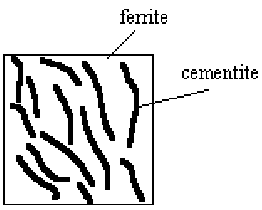
Let's start by just examining the solid region below the eutectic 723°C.
In the red region we have the alpha (α) phase. This is an unsaturated solid solution of iron and carbon called **FERRITE**. The iron in this phase is a body centres cubic crystal (BCC). The magnetic properties of this material are of particular importance.



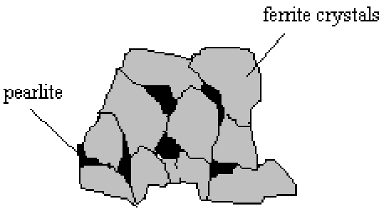
The green region contains hyper-eutectic steel commonly called mild steel. This is a solution of 87% ferrite and 13% cementite called **PEARLITE**. The microstructure is shown below.

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

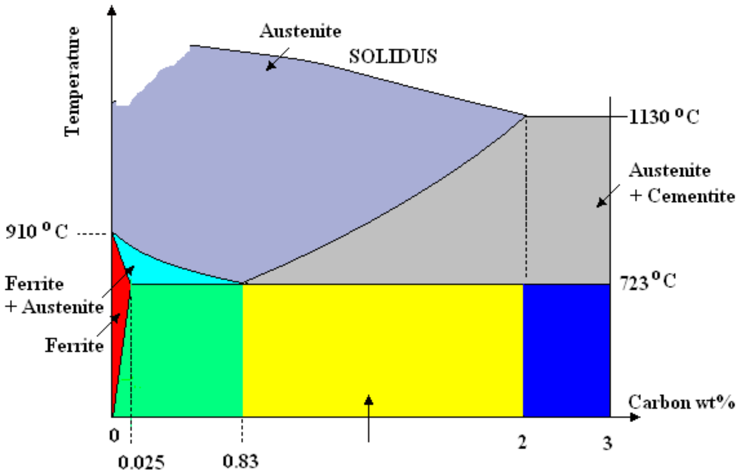
At higher quantities of carbon, the carbon starts to appear as free graphite and we have what is commonly called **CAST IRON**.

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.



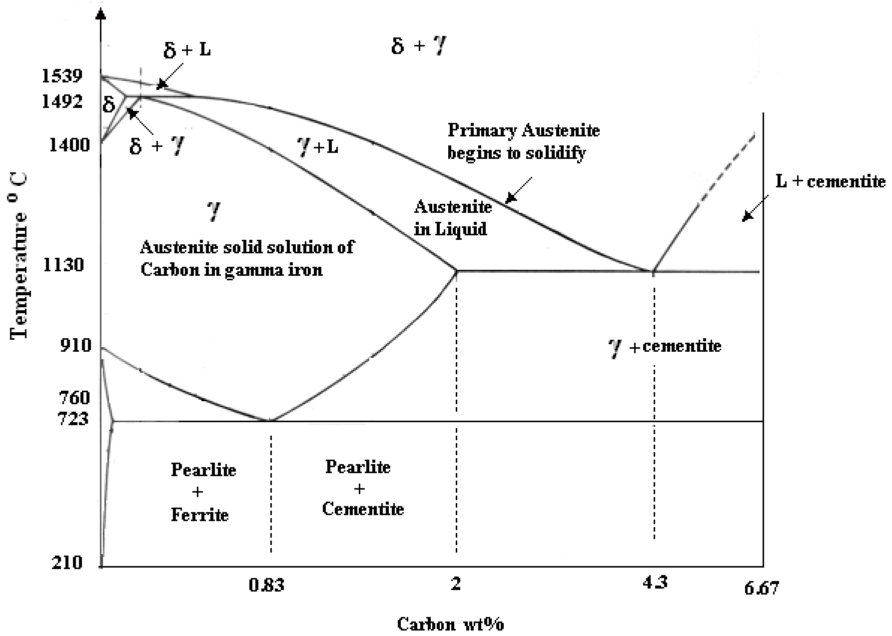
Note that we have a second eutectic point at 2%C and 1130^{o}C.

The microstructures are like this.

Austenite

Austenite with Cementite forming at the boundaries

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

AUSTENITE AND MARTENSITE

In the context of carbon steel this refers to two forms of the steel. When heated above the critical temperature, all the carbon diffuses into the iron to produce a uniform structure called Austenite. This has a crystalline structure of Faced Centre Cubic (FCC). When this is quenched the structure changes into Martensite with a crystal structure that is Body Centred Tetragonal (BCT). Martensite is not shown on the phase diagram because it is not a stable phase and is not produced by cooling slowly. Martensite is easily converted into Austenite by heating it. Heating allows the carbon to diffuse out of the crystal lattice and cementite/ferrite crystals form.

Other metals form structures that behave in the same way as iron/carbon and so the terms Austenitic and Martensitic are often applied to other metals to indicate the same process. It is found that Austenitic structures can be transformed into Martensitic structures by stress and strain as well as by heat. The crystalline changes produce distortion in the crystal lattice and dimensional changes in the bulk material. Heating can reverse this and this forms the basis of memory metals.

SELF ASSESSMENT EXERCISE No.2

1. Explain the meaning of the following terms.

   Ferrite
   Cementite
   Austenite
   Martensite
   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.