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Thermal Equilibrium Diagrams (Phase Diagrams)

Equilibrium may be defined as a state of balance of stability. When a metal solidifies, equilibrium will occur under conditions of **slow cooling** where the reduction in temperature is small in relation to the time elapsed (gone). To achieve equilibrium it would be necessary, at every stage of cooling, to give the alloy elements **time to diffuse** (mix through on another) which would lead to a state that each grain of metal would have the same composition throughout. Complete diffusion seldom takes place in casting because solidification usually takes place before diffusion is complete.

The Lever Rule

The equilibrium diagram for a solid solution alloy that we have just been dealing with contains two different phases, liquid and solid solutions. Between the liquidus and solidus lines these two phases exist together in equilibrium and hence the area between the curves is known as the two phase region. If a horizontal line is drawn through the two phase region, such a line is called a tie line. We see a tie line drawn in this equilibrium diagram. The lever rule may be introduced by considering the simple see-saw. For the see-saw to be balanced, i.e. in equilibrium, without movement up or down on either side, **(weight W1) (distance X1) = (weight W2) (distance X2).**

This is the lever rule and in metallurgy the horizontal constant temperature tie-line represents the see-saw with the fulcrum (hinge point) at the alloy composition under consideration. Therefore if we take the diagram for the (**Copper-Nickel**) alloy as in figure 5, and we take the composition of **60%** Copper and **40%** Nickel the lever rule will apply like this.

[Weight of solid solution of composition (q) / Weight of liquid of composition (m)]= bm / qb

Ratio = bm / qb

There are a number of different types of thermal equilibrium diagrams

1. Two metals completely soluble in each other in both liquid and solid states.
2. Two metals completely soluble in each other in the liquid but not in the solid state (**Eutectic alloy**).
3. Two metals completely soluble in each other in the liquid and partially soluble in the solid state.
4. Iron / Carbon equilibrium diagram.

1. Two metals completely soluble in each other in both liquid and solid states

Instead of dealing with several different cooling curves for any alloy, a quicker graph has been created using the various arrest points of all the alloys. When these points are marked on a graph and joined up we get a thermal equilibrium diagram which looks like this in figure below.

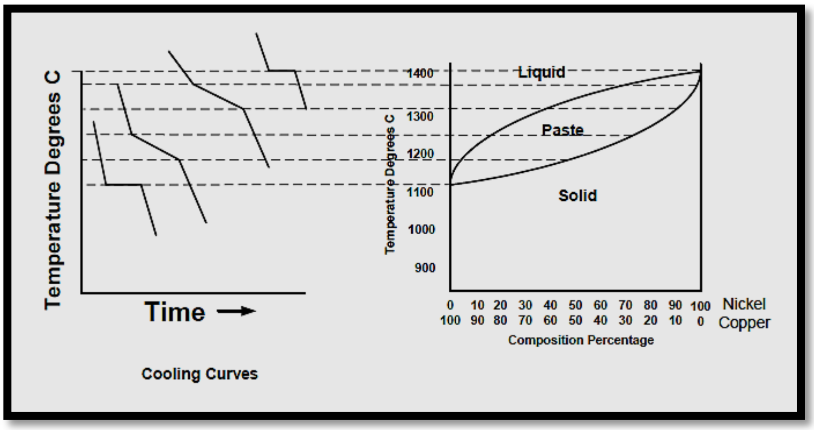

Figure 1. Creating a thermal equilibrium diagram.

As you can see there are three areas the **liquid state**, the **solid state** and the **pasty state** (consists of a solid phase and a liquid phase). A very important point to note is that the line joining all the points where the liquid begins to solidify is known as the **Liquidus line** while the line joining all the points where solidification is just complete is known as the **Solidus line**.

If we want to find out what temperature **60%** Copper is fully solidifies at in an alloy of Copper and Nickel. Firstly we need the thermal equilibrium diagram for the alloy of Copper and Tin. This is the thermal equilibrium diagram for the alloy of Copper and Nickel. In order to find what temperature **60%** copper solidifies at we simply draw a vertical line from **60%** copper until it hits the solidus line and at this is the point where **60%** Copper has fully solidified.

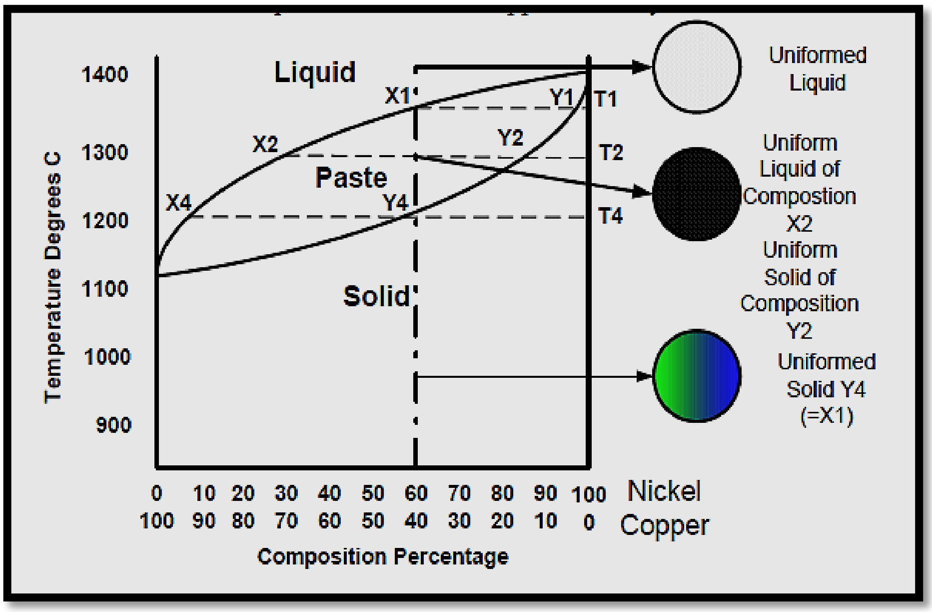

Figure 2. Nickel-Copper thermal equilibrium diagram.

2. Two metals completely soluble in each other in the liquid but not in the solid state (Eutectic alloy)

An eutectic is an alloy of lowest melting point in that alloy system and is formed when two different solid phases separate simultaneously at constant temperature from a single liquid phase (i.e. changing from a solid to a liquid at a constant temperature).

The solid solution equilibrium diagram discussed was formed by two metals being totally soluble in both the liquid and solid states. A Eutectic equilibrium diagram results when the two metals are soluble in the liquid state but insoluble in the solid state. In the liquid state the two metals are soluble in each other but when cooling is complete, the grain of the solid alloy consist of two distinguishable metals which can be seen under a microscope to be like a layer of one metal on top of a layer of the other metal. This state is completely different where the cooled solid grains look just like one metal when viewed under a microscope. In order to fully understand this type of alloy combination we will look at the (**Cadmium-Bismuth**) eutectic thermal equilibrium diagram. Cadmium and Bismuth are completely soluble in the liquid state, but are completely insoluble in the solid state.

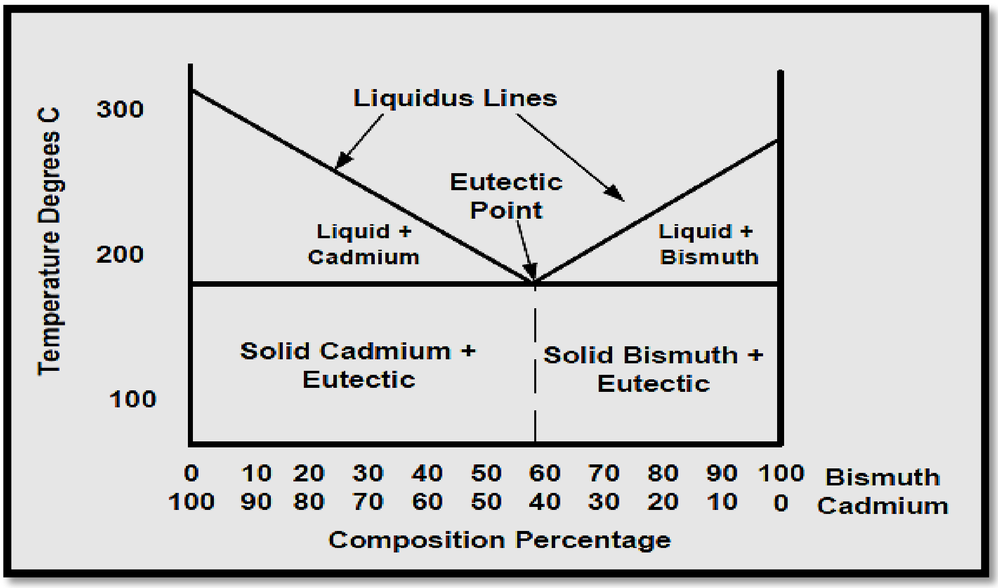

Figure 1. Bismuth-Cadmium (Eutectic Alloy).

The first and most noticeable point on this diagram is the **Eutectic point**. The eutectic point as can be seen above is a point in the diagram where the liquid alloy changes to a solid without going through a pasty state. This is the lowest melting point of any composition for the alloy.

As you would accept everything above the liquidus line is in the liquid state and in this state the two metals are totally soluble in each other. In the eutectic point region, there is only the eutectic composition alloy. If you look at **100%** Cadmium you will see that there is a large amount of solid Cadmium while this decreases in the alloys found nearer to the eutectic. The same applies for Bismuth. Therefore we can say that as the composition of the alloy moves away from the eutectic composition, grains of either Cadmium or Bismuth appear in the eutectic matrix.

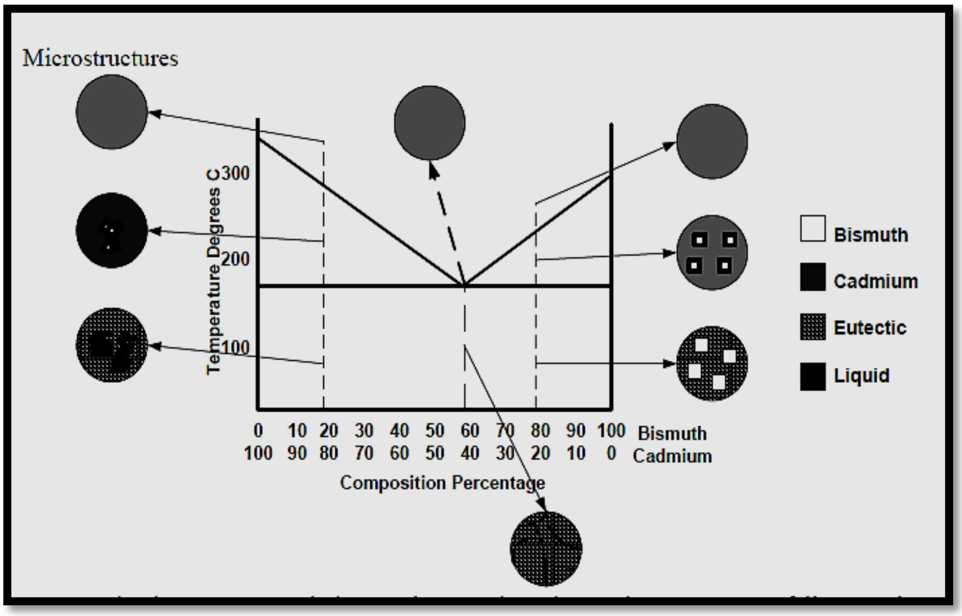

Figure 2. Bismuth-Cadmium (Eutectic Alloy).

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An examination at **80%** Cadmium and **20%** Bismuth. As the temperature falls crystal nuclei of pure cadmium begin to form. The temperature cuts the liquidus line at **(80/20)%** and the other phase boundary is the **100%** Cadmium ordinate. Dendrites of cadmium are deposited and the remaining liquid becomes increasingly richer in bismuth. Therefore the composition of the liquid moves to the right. As the temperature decreases more cadmium deposition takes place. The growth of Cadmium dendrites and consequent enriching of the remaining liquid is Bismuth.
The changing properties depending on metal composition are shown in figure below.

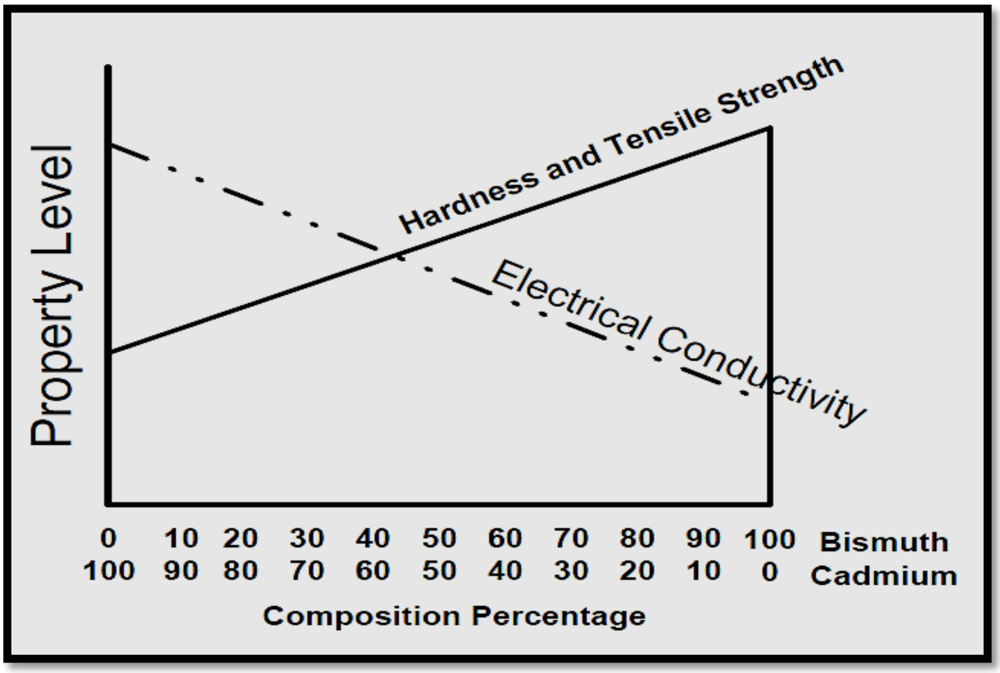

Figure 3. Metal Properties.

3. <u>Two metals completely soluble in each other in the liquid state and partially soluble in the solid state (Partial Solubility)</u>

The partial solubility equilibrium diagram is derived from the previous two diagrams that indicated soluble and insoluble states. <u>Few alloys exhibit total insolubility or total solubility and many metals combine to form a partial solubility system</u>. The ends of the totally soluble system are amalgamated with the central portion of the insoluble or eutectic system to form the partially soluble in the solid state equilibrium diagram as shown in figure below. The partial solubility diagram looks very different to what we have encountered (happened) so far so we will work on its various components before we move on to seeing its uses. (<u>**Lead-Tin**) combine to form solder and the equilibrium diagram is shown below</u>. On this diagram we have included drawing of a typical microstructure for six different alloys of (Lead-Tin) these microstructures are fairly self-explanatory further explanations can be gotten by clicking on the relevant microstructure in figure below.

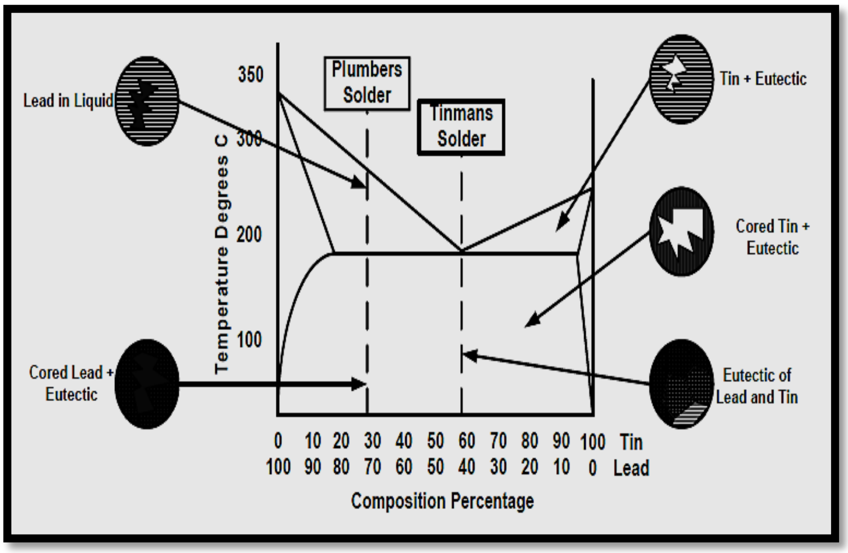

Figure 1. Lead-Tin (solder) partial solubility.

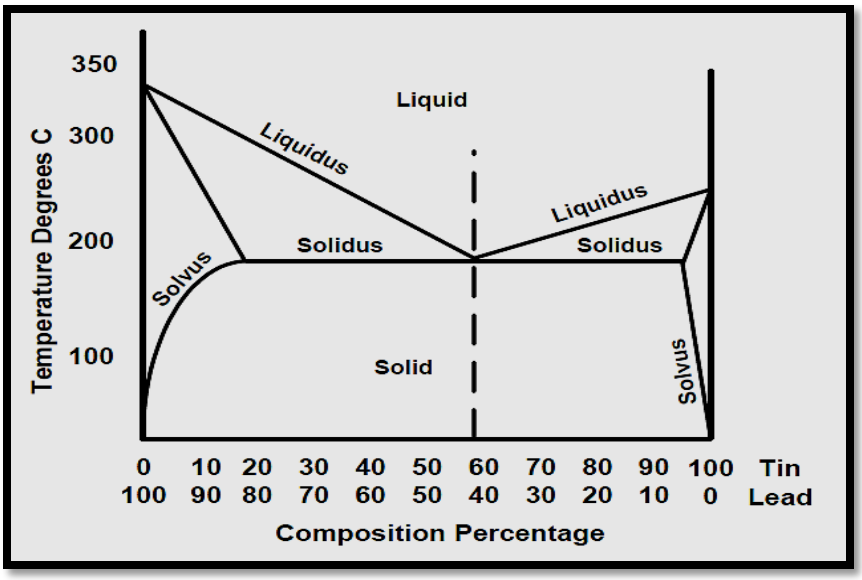

Figure 2. Liquidus and Solidus lines.

Inter-Metallic Compounds

Whilst some metal alloy systems exhibit total or partial solubility and others are insoluble in the solid state, a number of metals combine together to form an intermediate phase or intermediate compounds. There are two types of inter-metallic compounds which are often encountered (happen) in metallurgy. These compounds are usually **hard** and **brittle**.

1. Electron Compounds

These compounds are of definite chemical crystal structure and get up if the two alloying metals are of different crystal structure, valence, and if one of these metals is electro-positive with the other being electro-negative, an example of this type of electron compound would be an alloy of the elements (**Magnesium-Tin)** which combine to form an inter-metallic compound (**Mg_2Sn)**. The composition of the compound is fixed and consists of two atoms of Magnesium combining with one atom of Tin. Metallic compounds form a crystal lattice with the atoms of the alloying metals taking up specific positions within the lattice.

2. Interstitial Compounds

Interstitial compounds, as the name suggests form between metals, or metals and non- metallic elements, with atom sizes very similar to those that form interstitial solid solution. One set of atoms fit into the spaces or interstices, between the larger atoms. Iron Carbide (**Fe_3C**) or **Cementite** which is important in the study of (Iron-Carbon) diagrams is an example of an interstitial compound. As the chemical symbol for Cementite (**Fe_3C**), we know that **Cementite** is an interstitial compound containing **3** iron atoms for every **1** atom of Carbon.

The Allotropy of Iron

Allotropy is the ability of some elements to exist in different physical forms (differing in color, hardness, melting point etc.). Iron is allotropic; at room temperature pure iron exists in the **BCC** crystal form but on heating transforms to a **FCC** crystal. The temperature that this first transformation takes place is known as a **Critical Point** and it occurs at **910** degrees Celsius. This change in crystal structure is accompanied by shrinkage in volume, since the atoms in the **FCC** crystal are more densely packed together than in the **BCC** crystal. At the **Second Critical Point** the **FCC** crystal changes back to a **BCC** crystal and this change occurs at **1390** degrees Celsius.

- Iron below **910** degrees is known as alpha iron (**α**) **BCC.**
- Iron between **910** and **1390** degrees is known as gamma iron (**γ**) **FCC**.
- Iron above **1390** degrees is known as delta iron (**δ**) **BCC.**